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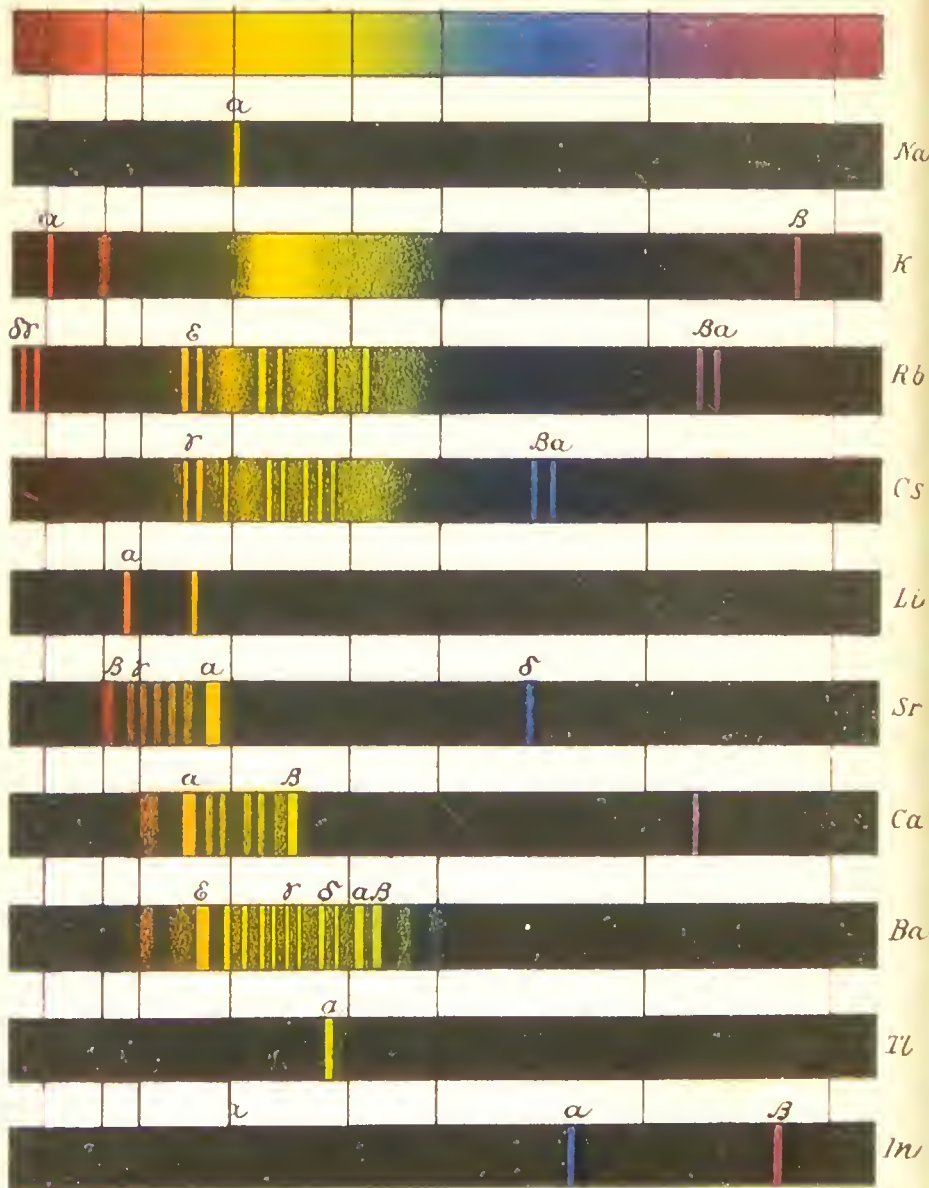
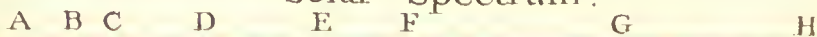
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TEXT-BOOKS OF SCIENCE

ADAPTED FOR THE USE OF

ARTISANS AND STUDENTS IN PUBLIC AND SCIENCE SCHOOLS.

QUALITATIVE CHEMICAL ANALYSIS AND LABORATORY PRACTICE.



QUALITATIVE CHEMICAL ANALYSIS

AND
LABORATORY PRACTICE

BY

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PREFACE.

THIS BOOK is divided into two distinct parts. In PART I. the student is instructed to perform a series of experiments, in order to familiarise himself with the leading properties of the chief non-metallic elements, and of the principal substances which they form by their mutual union. This portion of the book is, of course, supplementary to the work of the lecture-room, and should be studied in connexion with a manual in which the origin, properties, and relations of the various bodies are fully described.

The experiments are generally of a very simple nature, and are strictly illustrative of the chemical and physical properties of the substances to which they refer. To each lesson is appended a short statement or summary of the facts which that lesson is intended to convey. The object of these *résumés* is to afford the student precise ideas of the nature and extent of the information which he has gleaned from the experiments he has performed. The advantages of this preliminary course are manifest. Not only does the student become practically familiar with the properties of a large number of chemical agents, but he acquires opportunities for the exercise of manipulative skill and dexterity in the construction and arrangement of appa-

ratus, which the few and simple operations of ordinary qualitative analysis are not so well fitted to give. In arranging this course of laboratory practice we have sought to cover the Scheme of Practical Instruction sketched out in the Syllabus of the Science and Art Department.

PART II. treats of Qualitative Analysis ; it is divided into five sections.

In the first section the general preliminary operations of testing are described, such as the employment of flame reactions, the use of the Bunsen flame, the spectroscope, and so forth.

The second section treats of systematic qualitative testing. The wet and dry reactions of each of the more commonly occurring bases and acids, inorganic and organic, are first described, after which a synopsis of analytical methods is given.

The third section gives the special tests for the rarer elements, and shows where they may be expected, and how they may be separated, in the ordinary course of analysis.

The fourth and fifth sections have been added mainly for the use of medical students.

We have endeavoured to make this book as practical as possible. The methods of analysis are, of course, mainly founded on established and reliable processes. Still the book will be found to contain a number of novelties both in

the way of shortening the course of systematic testing and in the recognition of bodies by means of special tests. We have hesitated, however, to adopt new methods, unless experience has shown them to be preferable to the older ones. All the experiments described in the First Part have been carefully tried; and with the exception of certain of the separations of the rarer metals and organic poisons, which, however, will be recognised as well-established processes, all the operations described in the Second Part have been repeatedly tested by ourselves and by our students.

Our thanks are due to Mr. DUGALD CLERK and to Mr. STEPHEN MILLER for the attention they have bestowed on the woodcuts.

PREFACE TO THE EIGHTH EDITION.

A FEW omissions and some additions have been made in this edition. The Tables which serve as guides in Qualitative Analysis have been altered, and, it is hoped, improved. The symbol *Aq* is used to express an aqueous solution of the substance after the formula of which it is placed.

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EARTHS *To face Title-page*

QUALITATIVE
CHEMICAL ANALYSIS
AND
LABORATORY PRACTICE.

PART I.

*PREPARATION AND PROPERTIES OF GASES,
LIQUIDS, AND SOLIDS.*

LESSON I.

PREPARATION AND PROPERTIES OF OXYGEN.

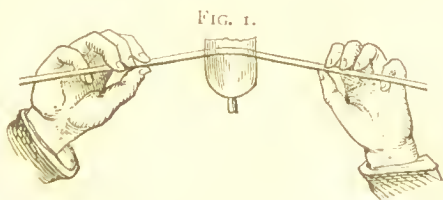
TAKE a few crystals of potassium chlorate, place them in a clean dry test-tube, and heat them gently over a small Bunsen flame (*see list of apparatus in Appendix*). The salt begins to spirt, then fuses. Now light a small splint of wood, blow out the flame so as to leave the wood just glowing at the point, plunge this into the tube in which you are heating the potassium chlorate; but do not allow the wood to touch the fused salt in the tube. Note what takes place: the splint, which only glowed when introduced into the tube, now bursts into bright flame, with a slight explosion. Withdraw the splint, blow out the flame, introduce it again into the tube; the same brilliant light will be noticed. What does this teach us?

That, by heating potassium chlorate, we have produced a substance having the property of causing an almost expiring flame to burn again more briskly than ever, which property, as we can easily determine, the potassium chlorate does not itself possess. This substance is oxygen gas. If this oxygen has been produced from potassium chlorate, then that salt must have undergone some change. Let us put this to the test. Take a few crystals of the chlorate, dissolve them in water in a test-tube (by shaking the tube, the mouth being closed by the thumb), and to this solution add a drop of a solution of silver nitrate. Nothing seemingly takes place, the liquid remains clear. Take now the small quantity of potassium chlorate which you have heated in the test-tube, dissolve this also in water, and add a drop of silver nitrate solution ; at once a white solid forms in the liquid, and this on shaking settles down to the bottom of the tube, (such a solid substance, produced by the addition of one solution to another, or, in some cases, by passing a gas into a liquid, is called a *precipitate*). These different actions of silver nitrate show us that the potassium chlorate has been changed by heat. What we have after heating is potassium chlorate *minus* oxygen, which, as we saw, goes off as a gas ($\text{KClO}_3 = \text{KCl} + \text{O}_3$).

In heating the potassium chlorate you will notice that it spirts, and gives up moisture, which, condensing on the colder part of the tube, is liable to flow back on to the hot portion, and so to crack the glass. Before preparing a quantity of oxygen it is therefore necessary to dry the salt. To do this, grind about 25 grams of potassium chlorate in a mortar, place it in a porcelain dish which is supported on a tripod over a very small flame, stirring it from time to time with a glass rod until it is dry. The temperature to which it is necessary to heat potassium chlorate before it parts with its oxygen is so high that the glass vessel containing the salt is very apt to crack, or at least to soften ; but by mixing with the chlorate a small quantity of an infusible substance, as

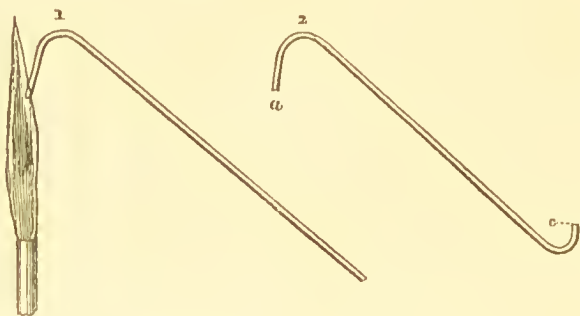
sand, oxygen will be given off at a comparatively low temperature. To facilitate the decomposition of the chlorate, we generally use not sand, but manganese dioxide, which acts more readily. Take about 5 grams of manganese dioxide and set it drying, as you have done with the potassium chlorate.

Meanwhile get ready an apparatus in which to prepare and collect the oxygen. Take a flask such as is described in the list of apparatus, No. 1, clean and dry it; to do this, pour a little water into the flask, add a few small pieces of filtering paper, rinse well, shake out the paper, rinse again with water, and let the flask drain; then heat it gently over a flame, turning it round, and either suck or blow out the heated air by means of a piece of glass tubing; select a good cork a very little larger than the neck of the flask, soften it (by wrapping it in a piece of paper, and rolling it several times under the foot upon the floor), and bore a hole in it about 6 mm. diameter, with a round file. (See Note 1, page 8.) Choose now a piece of glass tubing about 85 cm. long and very slightly wider than the hole in the cork. Light an ordinary gas-burner, bring the tube at about 15 cm. from one end into the flame, holding it parallel with the broadest part (fig. 1), and keep turning it round; you will soon feel the tube soften. Now slowly bend it, as if you were making a crook like a shepherd's staff, turning it in the flame as much as possible, and not hurrying the operation in the least. Some practice is required to make a neat bend; but if the flame be good, if you turn the tube incessantly, and if you bend it *slowly*, you will soon be able to conquer any little difficulty which at first may present itself. When bent, the tube should have the shape shown in fig. 2, No. 1. At about 15 cm. or so from the other end make



another bend in the opposite direction, but do not make this bend so sharp as the first (fig. 2, No. 2). In making this bend, hold the tube so that you may look along it, and then you will be able to make both bends in one plane. Now, by means of a three-cornered file, make a scratch on the tube about 10 cm. from the end (fig. 2, No. 2, c), and, by a sharp pull, break the tube at this point. Holding the tube in both hands, bring one end of it into a Bunsen's flame, the tube being inclined at an acute angle with the flame (see fig. 2, No. 1); keep turning it round until just the edge of the tube begins to glow, then after a few moments (turning the tube all the while) withdraw it, when you will find that the

FIG. 2.

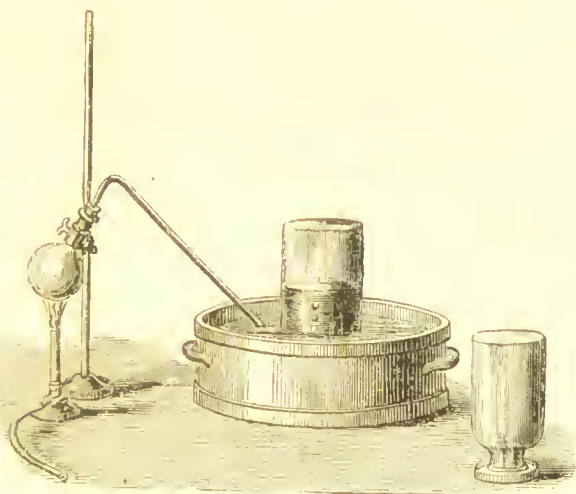


rough edge is now perfectly smooth; do the same with the other end of the tube, and allow it to cool. The end *a* (see fig. 2) is now to be gently fitted into the cork. By this time the potassium chlorate and manganese dioxide will be dry; these are mixed together in a mortar, the mixture placed upon a piece of paper, and poured, by means of this, into the flask. Fit the cork with the bent tube into the flask and support it by a clamp (see fig. 3).

To collect the gas, use the pneumatic trough and four gas bottles. The trough is nearly filled with water, in which a gas bottle is inverted so that the water may rush into it, the air escaping as the water enters. Some little

management is required to fill the bottle completely, but by raising the mouth—the bottle lying on its side beneath the water—just above the surface, and then slowly depressing it, the last bubble of air may be forced out. When this is done, place the bottle mouth downwards to one side of the trough, while you fill the other bottles in the same way. Now place the flask on the retort-stand in such a position that the lower end of the delivery tube passes under the water just beneath the hole in the beehive

FIG. 3.



shelf of the trough. Everything being now ready (see fig. 3), gently heat the flask, using at first a small flame; the air in the flask will be first of all expanded and driven out, bubbling up through the water in the trough. When the bubbles begin to follow one another in rapid succession they may be tested by bringing a glowing splint of wood over the place where they stream up through the water. If the splint bursts into flame, then we may begin to collect the gas. To do this, move one of the bottles on to the beehive shelf, so that its mouth is over the opening in this shelf; the gas will

then rise into the bottle, displacing the water, which finds its way into the trough. When full, depress the mouth of the bottle somewhat further beneath the water, slip a small tray under it, then lift the bottle, standing mouth downwards, on the tray (which must contain a little water) out of the trough, and set it aside.

Fill the other three bottles in a similar manner. In heating the flask while preparing the gas, so regulate the heat as to avoid any sudden rush of gas ; and whenever a sufficient amount of oxygen has been collected, remove the lamp and lift the end of the delivery tube out of the water, otherwise, as the flask cools, the water will rush back into it and crack it. The mass remaining in the flask may, when cold, be easily washed out with water.

We will now proceed to examine the properties of the oxygen we have obtained. By the preliminary experiment with potassium chlorate heated in the test-tube we have learned that a burning body when plunged into oxygen burns with greatly increased activity. *Oxygen is evidently a supporter of combustion.*

Experiment 1.—Take a small piece of amorphous phosphorus about the size of a pea, and place it in the cup of a deflagrating spoon, set fire to the phosphorus by bringing it into a gas flame, and plunge it into a bottle of oxygen : a brilliant white light, almost insupportably bright, is produced, together with dense white fumes. (If the gas bottle be made of thick glass, it is advisable to dilute the oxygen in it with about one-third of its volume of air before burning the phosphorus, as the great heat may crack the bottle. This may be done by depressing the bottle in the trough, allowing one-third of the oxygen to escape, and then lifting the bottle, mouth downwards, out of the trough, so that the water which flowed in when the oxygen escaped, may run out.) When the bottle is cool, remove the deflagrating spoon, put a little water into the bottle, and shake it up ; the white fumes dis-

appear, they are dissolved in the water. Taste a few drops of the solution thus formed ; you find it exceedingly sour or *acid*. Pour into the bottle a few drops of blue litmus solution (reagent list, No. 29) ; it turns red, showing the presence of an acid. What, then, has this experiment taught us ?

- (1) That many substances burn in oxygen with great eagerness.
- (2) That a substance having totally different properties from either oxygen or phosphorus is produced when these bodies combine together. The colourless gas oxygen and the red solid phosphorus form, when chemically combined, a light snow-like mass, which, when dissolved in water, gives rise to a solution possessing an intensely sour taste.

Experiment II.—Place a small piece of sulphur in the deflagrating spoon, set fire to it, and bring it into a bottle of *undiluted* oxygen ; it burns with a pale lavender-blue flame, considerably more brilliant than that noticed when sulphur burns in air. After the combustion is over, remove the spoon, and note the pungent odour of the substance formed, also the seeming absence of anything in the bottle ; the product of combustion is an invisible gas. Add a little water, shake the bottle, and pour in a drop or two of blue litmus solution. By its action on the litmus you see that an acid is present.

Experiment III.—In the third bottle a small piece of charcoal is burned, in the spoon. Note the comparatively feeble light produced ; the presence of the gaseous compound formed is shown (1) by its extinguishing a lighted taper when plunged into it ; (2) by its action on lime-water, which, when added and the bottle shaken, becomes turbid, owing to the gas in the bottle, known as carbon dioxide,

CO₂, combining with the lime (lime-water being a solution of lime in water), and forming a substance, carbonate of lime, or calcium carbonate, insoluble in water, and therefore appearing as a solid, floating about in small particles in the clear liquid, and thus rendering it turbid.

You have thus detected the presence of an invisible gas, by presenting to it something with which it could combine to form a new substance, having such characteristic properties as to be easily recognisable ; you have applied a *chemical test*.

You have learned from these experiments :—

- (1) That oxygen supports combustion.
- (2) That the production of substances differing in properties from the substances which combine to form them is a characteristic result of *chemical action*.
- (3) The meaning of the term *chemical test*.

The fourth bottle of oxygen is set aside, with its mouth downwards, in one of the small trays : we shall have occasion to use it in Lesson IV. As oxygen will be frequently used in the course of the following lessons it will be, on the whole, more convenient to fill a small gas-holder with the gas before proceeding to the next lesson.

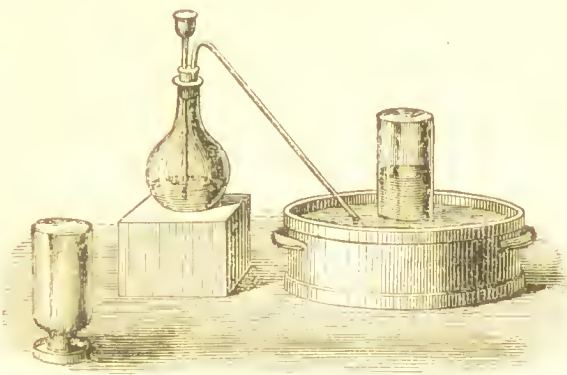
Note 1.—In boring a hole in a cork, do not forcibly drive the end of the file into the cork, but gently turn the file round, at the same time pressing it cautiously into the cork, until the hole is made ; take care that the hole is bored straight through, and not in a slanting direction. If you wish to enlarge the hole, you may easily do so by working the file round and round, filing away thin little bits of cork ; but see that you do this equally on all sides, otherwise the round glass tube will not perfectly fit the hole in the cork. Cork-borers, which are sold in sets, are very useful, making neater holes than a file.

LESSON II.

PREPARATION AND PROPERTIES OF HYDROGEN.

TAKE one or two grams of zinc, put them into a test-tube, and add a few drops of dilute sulphuric acid ; you notice an effervescence, bubbles of gas make their way through the liquid ; bring a lighted taper into the test-tube : a slight explosion takes place, and you see a momentary flash, as if something in the tube had taken fire.

FIG. 4.



You have here another instance of chemical action : the zinc has so acted on the sulphuric acid as to decompose or break it up, hydrogen gas, one of the constituents of the acid, being evolved. You must now proceed to prepare and collect a quantity of hydrogen, making use of the reaction you have just learned for this purpose.

Take a flat-bottomed flask (similar to that represented in fig. 4), holding about 300 c.c.; select a cork, soften it, and bore in it two holes of such a size as to fit the bent tube you used in the last lesson. In boring the holes, take care you do not make them too near the edges of the cork, nor too near one another, otherwise the cork will be sure to

crack when you attempt to fit it into the mouth of the flask. Into one of these holes you fit the bent delivery tube, and into the other a straight glass tube, terminating at its upper end in an open mouth-shaped funnel ; this funnel-tube is to be pushed through the cork, so that when fitted into the flask it reaches very nearly to the bottom. Take now about 30 grams of granulated zinc (see reagents list), put it into the flask, inclining the flask to one side, and gently sliding the zinc down the neck, taking care that it does not fall heavily against the bottom, else it will most likely crack the flask ; fit the cork into its place, and arrange the apparatus so that the delivery tube may reach under the shelf of the trough (fig. 4).

Pour into the flask through the funnel-tube sufficient water to cover the zinc to the depth of about 6 mm. or so ; then add, also through the funnel, a small quantity of diluted sulphuric acid (one part acid to four water, previously mixed and allowed to cool), and shake the flask gently ; in a minute or two you will notice an effervescence ; gas begins to bubble up through the water in the trough ; after a few moments add a little more acid, so that a pretty rapid stream of gas may be obtained. Do not, however, add much acid at a time, otherwise the action will become violent, the liquid will get very hot, and will froth up through the funnel-tube ; should there be indication of this, pour a little water into, and also on to the outside of, the flask, in order to cool it. Take a test-tube, fill it with water in the trough, and bring it, mouth downwards, over the hole in the shelf whence the gas is issuing ; when it is full of gas, cover the mouth of it with the thumb (while still in the trough), lift it mouth downwards out of the water, remove the thumb, and bring a lighted taper to the mouth of the tube ; if an explosion ensues, the hydrogen is not pure, it is still mixed with air ; repeat this experiment after the expiration of a minute or so, and do not begin collecting the gas in bottles until a small quantity in a test-tube does not explode when brought near

a light, but takes fire and burns quietly. When you have satisfied yourself that the hydrogen is unmixed with air, proceed to collect four bottles of it, exactly as described in the last lesson.

Be careful never to bring a light near a mixture of hydrogen and air in a glass vessel, as if these gases are present in any quantity, and the vessel is not very strong, a dangerous explosion may occur.

Let us now examine some of the properties of this gas hydrogen, and see what lessons it has to teach us.

Experiment I.—Take a bottle of hydrogen from the little tray, hold it mouth downwards, and apply a light to the mouth of the jar; the gas takes fire, burning with a very pale non-luminous flame; pass the taper further up into the jar, it is extinguished. Hydrogen therefore differs from oxygen in being itself combustible, but not (under ordinary circumstances) a supporter of combustion. You may naturally inquire, Why keep the bottle of hydrogen inverted? The next experiment will answer this question.

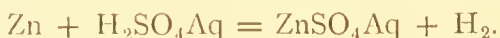
Experiment II.—Take the second bottle of hydrogen, lift it from the tray, keeping it inverted, in the right hand, while in the left you hold, also mouth downwards, the bottle in which you performed Experiment I., containing now only air; by tilting up the top of the bottle containing hydrogen, and holding the empty bottle as if you were pouring from the lower one into it (see fig. 5), you can in a very few moments decant all the hydrogen upwards into the higher bottle. Set the bottle from which you have poured the hydrogen, mouth downwards, in the tray; light a taper and bring it to the mouth of the second bottle, still held inverted in the left hand: a slight explosion ensues, and you see the pale lambent flame of burning hydrogen. Now apply a light to the mouth of the other bottle—the taper burns quietly, as if in air, showing you that all the hydrogen

FIG. 5.



has been poured out of this bottle. You learn then that hydrogen is much lighter than air, quickly rising through it. Had you held the bottle in Experiment I. mouth upwards, the light hydrogen would have escaped before you could have noticed its characteristic flame.

Filter the liquid contained in the flask used in these experiments into a small porcelain basin, evaporate it over a flame to about one-half or one-third its bulk, and set it aside ; when the liquid is cool, you will find a mass of white crystals formed in it ; this white solid is zinc sulphate, the second product of the action of zinc on sulphuric acid, the first being the hydrogen you collected. The action is thus represented :



You have learned from these*experiments—

- (1) That hydrogen is a combustible gas, burning with a feebly luminous flame.
- (2) That hydrogen is an exceedingly light substance, so light that it can be poured *upwards*.
- (3) That hydrogen and air form an explosive mixture.
- (4) That the action of zinc on diluted sulphuric acid is to produce an invisible gas, hydrogen, and a white crystalline solid, zinc sulphate.

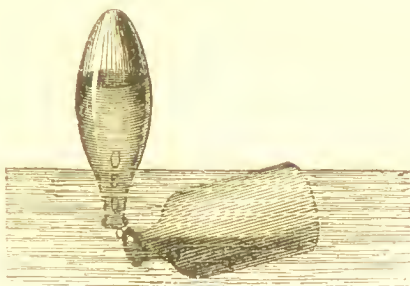
LESSON III.

COMBINATION OF OXYGEN WITH HYDROGEN.—MEANING OF THE TERMS ‘COMBUSTIBLE’ AND ‘SUPPORTER OF COMBUSTION.’

Experiment I.—Procure an ordinary soda-water bottle and a cork to fit it tightly ; fill it with water, pour out this water into a measuring glass—you thus find the capacity of

the bottle ; divide this by three, and now pour into the bottle one-third of the water which you know is required to fill it. With a file make a mark on the outside of the bottle on a level with the surface of the water inside. You have thus divided the bottle into two parts : one equal to one-third, the other equal to two-thirds, of the whole. Again fill the bottle with water at the trough, invert it, and let it stand on the beehive shelf, with its mouth under water. You now bring to the side of the trough the bottle of oxygen which you prepared but did not use in Lesson I., also a bottle of hydrogen from last lesson. Lift the bottle of oxygen, with the tray on which it stands, into the trough ; when the

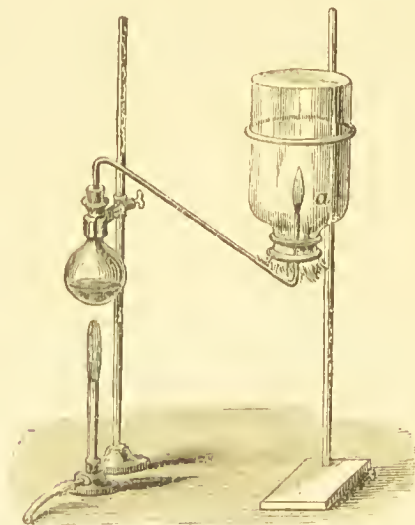
FIG. 6.



mouth of the bottle is beneath the surface of the water, withdraw the tray, gently depress the upper end of the bottle (held in the right hand), while with the other hand you hold the soda-water bottle so that the bubbles of oxygen as they escape may pass up through the water into it (see fig. 6). A little dexterity is necessary in thus decanting the gas up through the narrow neck of the soda-water bottle ; do not be too hasty, but allow the gas to pass up slowly and steadily. Fill the soda-water bottle with oxygen up to the mark you made with the file, that is, one-third ; then set it on the beehive shelf while you again bring the tray under the mouth of the oxygen bottle and lift it from the trough. Decant (as you have just done with oxygen) hydrogen sufficient to entirely fill the soda-water bottle, and set aside

any hydrogen which remains. Quickly cork the soda-water bottle, shake it, wrap it in a towel, withdraw the cork, and apply a light to the mouth of the bottle—a sharp, loud explosion instantly ensues. With the oxygen and hydrogen remaining, again fill the bottle, but this time vary the proportion of the gases—put less oxygen and more hydrogen, or *vice versa*; you will find that the explosion is less violent than in the first experiment.

FIG. 7.



The application of the light has caused chemical combination to take place between the two gases, oxygen and hydrogen; this combination is of a very violent nature, as testified by the loudness of the explosion. The product of the combination is water, which is composed of oxygen and hydrogen in the proportion of one volume of the former gas to two volumes of the latter. From the small volume of the gases employed, the quantity of water produced is so minute that it seemingly adds nothing to the drops already adhering to the inside of the soda-water bottle. If, however, we were to fill a very large and perfectly dry bottle with the two gases mixed in the above proportion and explode the mixture, we

should notice that a perceptible quantity of water formed as dew on the sides of the bottle.

With the fourth bottle of hydrogen prepared in last lesson you have another experiment to perform.

Experiment II.—Set up again the flask with bent delivery tube for the preparation of oxygen, putting into it a mixture of about 15 grams of potassium chlorate, and 3 grams of manganese dioxide, as directed in Lesson I. Soften the end, fig. 7, of the delivery tube in the flame, and keep turning it round until the edges run together, and so make the orifice much narrower than it originally was. Support the flask on a stand, so that the end of the delivery tube points straight upwards, and is about 20 cm. from the table. (No trough is needed in this experiment.)

Heat the flask gently, so as to produce a slow current of oxygen gas; from time to time bring a smouldering splint of wood near the end of the tube, and when the nearly expiring flame just bursts again into brilliancy, you may consider the stream of oxygen to be issuing with sufficient rapidity. Now lift the bottle of hydrogen, mouth downwards, from the tray; apply a light to it, and while the hydrogen is burning, place the mouth of the jar over the end of the tube from which oxygen is issuing. As you do this, you notice that at the point where the oxygen meets the burning hydrogen a long flame of ignited oxygen shoots up within the bottle (fig. 7).

If the oxygen is issuing in a rapid stream, there is danger of the flame produced by it being so large as to strike against the upper part of the bottle and crack it. You must, therefore, carefully regulate the supply of oxygen. The experiment is more easily performed by delivering the oxygen from a gasholder.

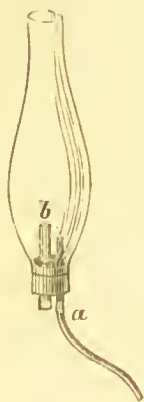
In this experiment you see that a gas which you had previously regarded as a supporter of combustion can itself be made to undergo combustion. As combustion is a *chemical combination* attended with evolution of light and heat, this action takes place where the two substances which combine

meet each other ; but the oxygen rushes into an atmosphere of hydrogen which surrounds it on all sides ; the particles of oxygen, as they are combining with those of hydrogen, are carried quickly forwards, and thus it is that the oxygen appears itself actually to burn within the hydrogen with the long narrow flame which you noticed.

The relativity of the terms ‘combustion’ and ‘supporter of combustion’ may be shown with gases other than pure oxygen and hydrogen. Thus air may be made to burn in an atmosphere of coal gas.

Take an ordinary lamp-cylinder, and fit it with a cork and tubes in the manner represented in fig. 8. Send a cur-

FIG. 8.



rent of coal-gas into the cylinder through the tube *a* ; in a minute or two the apparatus will be completely filled with the coal-gas ; now pass a lighted taper up the open wide tube *b* ; a bluish flame will form and continue to burn at the end of the wide tube so long as the current of coal-gas is maintained.

The formation of this flame is accounted for by reasoning similar to that used in explaining the burning of oxygen in hydrogen ; in this case air takes the place of oxygen, and the atmosphere of hydrogen is replaced by one of coal-gas.

You thus see that if a room were filled with coal-gas and the gas-pipes with air it might still be possible, by proper means, to obtain a light at the burners. The air in this case would appear to be a combustible gas, and the coal-gas would seem to support its combustion. These experiments also afford us information concerning the nature of flame. We see that a flame is produced by the union of two gases, which in the act of combination develope so much heat that their products whilst still gaseous are incandescent. It will be now clear why the flame of the taper was extinguished when it was pushed up into

the mass of the hydrogen gas and why the whole body of the gas did not instantaneously inflame in contact with the light. The flame of the taper was extinguished because the material of the taper had no power to combine chemically with the hydrogen ; the hydrogen itself did not, as a whole, inflame, because there was no oxygen with which it could combine : it only burnt at the mouth of the jar, where it met with the air.

In this lesson you have learned :—

- (1) That oxygen and hydrogen unite together violently when brought near a flame.
 - (2) That the union of two volumes of hydrogen with one volume of oxygen gives a louder explosion than occurs by inflaming any other proportionate mixture of these two gases.
 - (3) That water is composed of oxygen and hydrogen in the above proportion, viz., two volumes of hydrogen and one volume of oxygen.
 - (4) That the terms ‘supporter of combustion,’ and ‘combustible,’ are merely relative, and denote no absolute property of bodies.
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LESSON IV.

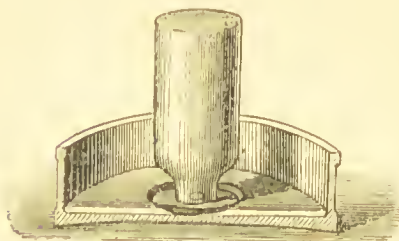
PREPARATION AND PROPERTIES OF NITROGEN.

THE gas nitrogen exists already made in the air ; in order to obtain it, you have only to take away another gas—oxygen—with which it is mixed.

Fill the trough to the depth of about 3 cm. with water, and place in it an ordinary white plate. Into this plate pour a little water coloured blue by the addition of litmus solution. (See fig. 9.)

Float a small porcelain dish, about 5 cm. diameter,

FIG. 9.



on the water,—the lid of a porcelain crucible, fastened to a piece of wood of sufficient size to float it, does very well. Place a little piece of amorphous phosphorus on the dish, and set fire to it by touching it with a hot wire. Have at hand

a large stoppered bottle, holding about 750 c.c. Take out the stopper, and place the bottle cautiously over the dish containing the burning phosphorus. You notice that as the phosphorus burns, the water rises slightly inside the bottle, showing that something is being taken away from the enclosed air. That it is the oxygen which is thus taken up by the phosphorus, is evident from the fact that the blue colour of the water gradually changes to red. This, you remember (Lesson I.), is owing to the formation of an acid, the product of the union of phosphorus and oxygen. When the combustion is over, and the bottle is cool, fill up the trough with water (take care that the bottle does not

upset as you do this), and decant the air or gas into two gas bottles (see Lesson III.).

Experiment I.—Plunge a lighted taper into one of the bottles ; the flame is at once extinguished, and the gas does not take fire. Nitrogen therefore is incombustible, and is a non-supporter of combustion.

Experiment II.—Into the other bottle pour a few cubic centimetres of clear lime-water, close the bottle with the palm of the hand, and briskly agitate it. The lime-water is not rendered turbid. This test serves to distinguish nitrogen from carbon dioxide, which, as you learned from Lesson I., extinguishes flame, but gives a precipitate with lime-water.

You learn then—

- (1) That air contains oxygen and nitrogen.
- (2) That by burning a combustible substance in a confined space of air, the oxygen is withdrawn (the combustible uniting with it), and nitrogen remains.
- (3) That this nitrogen possesses no very distinctive qualities, being neither combustible, nor supporting combustion.

LESSON V.

PREPARATION AND PROPERTIES OF NITRIC ACID.

CHOOSE a stoppered retort, capable of holding about 250 c.c., having a tolerably long beak ; clean and dry it. Weigh out 30 grams of potassium nitrate, place it on a small piece of paper turned up at the edges, so as to form a kind of little trough, and by means of this transfer it to the retort, taking care that none of it gets into the neck of the retort (see fig. 10). We act on this nitre with sulphuric acid ; the equation expressing this reaction is—

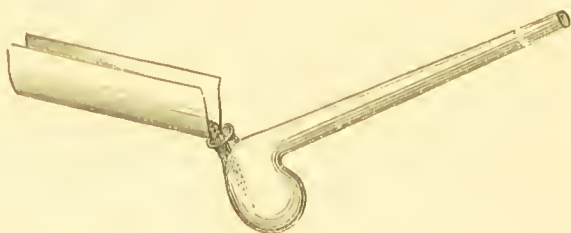
$\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{KHSO}_4$ —that is to say,
 $39 + 14 + 48 = 101$ parts by weight of potassium nitrate
 are decomposed by—

$2 + 32 + 64 = 98$ parts by weight of sulphuric acid ;
 one of the products being—

$1 + 14 + 48 = 63$ parts by weight of nitric acid.

Calculate then the amount of strong sulphuric acid required to decompose the 30 grams of nitre, weigh out this amount in a small beaker, and pour it into the retort through a small funnel passing well into the body of the retort through the opening at the neck. Put in the stopper and support the retort, with wire gauze beneath it, on one ring of a retort-stand, bringing another ring over the neck. Clean and dry a small flask, the neck of which will permit the

FIG. 10.



beak of the retort to be passed through it ; support it on the beehive shelf, and fill the trough with water, so that the flask may be pretty well covered, but take care that no water gets into it.

The apparatus has now the appearance shown in Fig. 11. Gently heat the retort : an action evidently goes forward ; after a little time brown fumes are evolved, and drops of liquid form on the sides of the neck, and trickle slowly down it into the small flask, or *receiver*, which being kept cool by the water surrounding it, condenses the nitric acid, which in the heated retort is in a gaseous state.

In the receiver a brownish-yellow heavy liquid, fuming

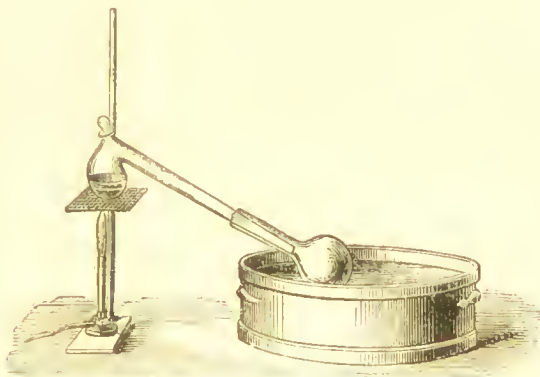
in the air, gradually accumulates ; this is concentrated nitric acid, which we will now examine.

When you have removed the light, pour out the semi-liquid contents of the retort, consisting chiefly of hydrogen potassium sulphate (HKSO_4), into a small basin. After cooling and solidifying, break up this salt into little pieces, and preserve it in a stoppered bottle.

You already know what is meant by a *chemical test*. In the laboratory we often have occasion to detect this substance nitric acid, and to do this we use certain chemical tests.

Experiment I.—Pour a little of the acid into a test-tube,

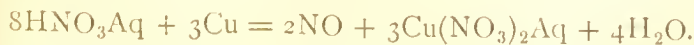
FIG. 11.



add a few drops of water, and then put into the tube a little slip of copper foil ; you notice that a violent action ensues, a dark reddish-brown gas is given off, and the liquid becomes more or less green in colour.

The production of these red fumes when a piece of copper foil is brought into contact with a liquid suspected to be nitric acid, is one proof that the liquid *is* nitric acid.

The red-coloured gas consists chiefly of nitrogen dioxide, NO_2 —



The NO thus formed, in contact with air takes up

another atom of oxygen, forming the ruddy-coloured gas NO_2 . But we have by the production of these same ruddy fumes, and the application to them of another chemical test, a much more delicate means of detecting the presence of small quantities of nitric acid.

Experiment II.—Take a few crystals of *ferrous sulphate* and dissolve them in a little *cold* water, in a test-tube. Into

FIG. 12.



the test-tube used in Experiment I. pour a few drops of nitric acid, so as to cause a fresh evolution of gas. Now hold the two tubes so that the ruddy fumes may fall into that containing the ferrous sulphate solution (see fig. 12); the clear solution becomes rapidly darkened in colour, until it is nearly black; this darkening effect of the oxides of nitrogen, when brought into contact with ferrous sulphate solution *in the cold*, is the second and most delicate test for the presence of nitric acid. (Boil the dark brown solution in ferrous sulphate; you see that the colour is almost entirely discharged. You now perceive why directions have been given to apply this test in cold solutions.)

To carry out the test—

Experiment III.—Make a solution of nitre in a little water in a test-tube; add to this a few crystals of ferrous sulphate. Shake the tube, incline it to one side, and cautiously pour a few drops of strong sulphuric acid down the side of the tube, so that the heavy acid may sink to the bottom, and there form a separate layer. At the point of contact of the two layers you will notice a dark brown-coloured ring: this is proof of the presence of nitric acid; it is nothing else than the dark liquid you produced in the last experiment by decanting nitrous fumes into a ferrous sulphate solution. The reaction which goes on in the tube is as follows:—The sulphuric acid acts on the nitre, nitric acid and potassium sulphate are formed; part of the *ferrous* sulphate acts on the nitric acid, robbing it of some of its

oxygen, ferric sulphate and lower oxides of nitrogen are produced ; the latter dissolve in the excess of ferrous sulphate, and this solution, as you know, has a dark brownish-black colour. In applying the test, be careful to have all the solutions perfectly cold ; by pouring the acid gently down the side of the tube, you do not allow it to mix with the liquid, because if it did so, heat would be produced, and the dark colour destroyed, as you learned in Experiment II.

In this lesson you have learned—

- (1) How to conduct a process of distillation.
- (2) That by the action of sulphuric acid on potassium nitrate, nitric acid is produced.
- (3) That this acid is a heavy, slightly coloured liquid, fuming in the air.
- (4) What are the tests for nitric acid, and what is the mode of their application.

LESSON VI.

PREPARATION AND PROPERTIES OF NITROUS OXIDE.

TAKE the nitric acid remaining from last lesson, put it into a porcelain basin, dilute it with a little water, and add ammonia to it (stirring with a glass rod after each addition of ammonia), until a drop taken on the end of a rod just ceases to redden blue litmus paper. Set the basin on a piece of wire gauze resting on a tripod-stand over a flame, and evaporate down until the liquid becomes slightly viscid, and no longer exhibits signs of ebullition. During this evaporation add from time to time a few drops of ammonia, otherwise the solution becomes acid, and when you heat the ammonium nitrate formed you find red nitrous fumes produced. Set the basin aside—as the liquid cools it

becomes solid. When quite cold, break up the solid substance in the basin into small pieces.

In this process you have *neutralised* the nitric acid by means of ammonia, the acid and alkali have combined together, the resulting *new* substance being ammonium nitrate—the white salt in the basin. The substance produced by the union of an acid with a base is called a *salt*. As a salt has a definite chemical composition, there must be a point reached, in adding ammonia to the acid, at which all the acid present is taken up by the ammonia; this is the *point of neutralisation*.

Put into a flask, which can be fitted with a delivery tube (that used in the preparation of oxygen may be employed), 10 grams of the ammonium nitrate which you have just made. Set the flask, fitted with its cork and tube, on the retort-stand, and arrange the trough in the usual manner, but use *warm water* instead of cold.

Heat the flask gently until the salt fuses, then gradually increase the heat until the fused ammonium nitrate begins to decompose with effervescence, and bubbles of gas succeed each other rapidly through the water in the trough. Allow a few minutes to elapse, then begin to collect the gas; fill three bottles, and set them aside on the small trays. In heating the flask, do not let the temperature get too high; if you see many white fumes appearing in the flask—especially towards the close of the operation—the heat must be moderated; but do not withdraw the lamp entirely, or, as the flask cools, the water may rush back from the trough into it, and crack it.

By the action of heat ammonium nitrate is decomposed, nitrogen monoxide is given off, and water remains; you may see this water condensing in the neck of the flask, and trickling down the sides— $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. This nitrogen monoxide is slightly soluble in cold water, but much less so in hot water, hence the reason for using warm water in the trough.

Experiment I.—Lift one of the bottles from the tray, set it, mouth upwards, on the table, and plunge into it a lighted taper ; the flame burns more brilliantly, but the gas itself does not take fire. Do this experiment quickly, and immediately replace the bottle, inverted, on the tray.

Experiment II.—For this experiment you must pass the deflagrating spoon through a cork of a size to fit the mouth of the bottle ; below the cork on the spoon is fitted a small copper or tin plate, which prevents the burning phosphorus from setting fire to the cork. (See fig. 13.)

Place a small piece of phosphorus on the deflagrating spoon, set fire to it, and plunge it into the jar of gas used in the last experiment, fitting the cork on the spoon into the bottle. The phosphorus burns very brilliantly, with almost as bright a light as when it burned in oxygen.

This confirms the teaching of the last experiment. When the fumes produced in this experiment have somewhat subsided, plunge a lighted taper into the jar ; it is extinguished, the gas behaves therefore as nitrogen does : now pour a little blue litmus solution into the bottle, close the mouth with the palm of the hand, and shake well ; the litmus is reddened, therefore an acid has been produced in this experiment. This result agrees with that obtained by burning phosphorus in pure oxygen (Lesson I.) or in air (Lesson IV.). But there is a difference between the powers of supporting combustion possessed by nitrous oxide and oxygen.

Experiment III.—Place a small piece of sulphur on the spoon, set fire to it, but let it be only just lighted and no more ; now bring it into the second bottle of nitrous oxide : the flame is extinguished. Had you employed oxygen in this experiment, you know that the sulphur would have burned with increased brilliancy.

FIG. 13



These combustions in nitrous oxide are due to the fact that the body burning decomposes the gas, taking to itself the oxygen ; but as there is a large quantity of nitrogen present, this dilutes the oxygen, and so the combustion is less violent than if it took place in oxygen alone. The oxygen and nitrogen being held together chemically, the low temperature of the burning sulphur was not sufficient to dissolve their union, the sulphur could get no oxygen, hence its flame was extinguished ; but if you heat the sulphur considerably above its melting-point before plunging it into the gas, it will burn brilliantly.

A mixture of oxygen and nitrogen would diminish the intensity of combustion like the oxide of nitrogen ; but to show the difference between such a mixture and nitrous oxide we will perform another experiment.

Experiment IV.—Pour a little cold water quickly into the third bottle of the gas, close the mouth with the hand, and agitate briskly ; invert the bottle, still keeping the hand over the mouth, and bring it thus beneath cold water in a basin. Now withdraw the hand : you notice that the water rises in the bottle, thus showing that you have dissolved some of the gas in the water you added. Again slip the hand beneath the mouth of the bottle, lift it, containing water, out of the basin, agitate briskly and replace it in the basin as before ; the water rises further in the bottle. Repeat this agitation until the water nearly fills the bottle. You now perceive how uneconomical it would have been to have collected the gas over *cold* water. This solubility in water also serves to distinguish nitrous oxide, which is a chemical compound of oxygen with nitrogen, from a mechanical mixture of these gases which would not dissolve in water to the same extent.

You learn in this lesson—

- (1) By what reaction nitrous oxide is produced.
- (2) That this gas has the power of supporting combustion, and in what way it does this.

- (3) That there is a difference between this gas and oxygen in their respective powers of supporting combustion.
 - (4) That there is a difference between a mechanical mixture and a chemical compound.
 - (5) That nitrous oxide is soluble in cold water.
 - (6) Something about the meanings of the terms 'neutralisation' and 'salt.'
-

LESSON VII.

PREPARATION AND PROPERTIES OF NITRIC OXIDE.

INTRODUCE about 30 grams of copper in small pieces into a flask which is fitted with a delivery and funnel tube in the manner represented in fig. 4. Mix 60 c.c. of water with the same amount of concentrated nitric acid, and pour some of this mixture on to the copper clippings through the funnel tube. Action evidently goes forward in the flask, for it is almost immediately filled with red vapours, and bubbles of gas make their way through the water in the trough; the red vapours in the flask soon however almost entirely disappear. Now begin to collect the gas which is coming over, and fill five bottles with it. This gas is produced by the above action without heating the flask. Should the action become too violent, pour a little cold water on the outside of the flask; if the stream of gas slackens, add a little more of the dilute nitric acid.

Experiment I.—Plunge a lighted taper into one of the bottles; the taper goes out, and the gas does not take fire: you notice, however, that ruddy fumes appear in the bottle. The formation of these will be explained by the fourth experiment.

Experiment II.—Place a small piece of phosphorus on the spoon, light it, and plunge it, *immediately* it begins to

burn, into the second bottle of the gas ; the burning phosphorus is extinguished. Nitric oxide does not support combustion as nitrous oxide does. If you repeat this experiment, allowing the phosphorus to burn briskly for a little time before you bring it into the gas, holding it for a few moments in the Bunsen flame, it will burn with increased brilliancy in the nitric oxide. You thus see that the temperature at which nitric oxide is decomposed and made to part with its oxygen is considerably higher than that at which nitrous oxide is similarly split up ; the latter therefore much more readily supports combustion than the former gas.

Experiment III.—Into the third bottle of nitric oxide plunge a piece of brightly-burning sulphur, held in the deflagrating spoon : it is extinguished. In nitrous oxide under the same circumstances the sulphur continues to burn.

Experiment IV.—For this experiment you will require a small bottle of oxygen (if you have not a supply in the gas-holder, make this as directed in Lesson I., using a smaller flask, and about 10 grams of potassium chlorate with 2 grams of manganese dioxide). Decant about one-fourth of the nitric oxide contained in the fourth bottle into another gas bottle, by means of the trough, and very slowly pass up into this a little oxygen. As each bubble of oxygen comes into contact with the nitric oxide, brown ruddy fumes are produced. After the addition of a small quantity of oxygen, shake the bottle containing the mixed gases (taking care not to let its mouth get above the water, else air will rush in) ; the water rises in the bottle, showing that gas is being dissolved. Continue the addition of oxygen, and at intervals shake the bottle ; you find that at last it is entirely filled by the water. You would naturally expect that by the addition of one gas to another the volume of gas would be increased ; in this case, however, it is diminished until it is actually *nil*. The reason is that the oxygen combines with the nitric oxide, forming nitrogen dioxide, NO_2 , a gas of a brown colour—hence the brown fumes in the flask when you prepared nitric oxide, and in the

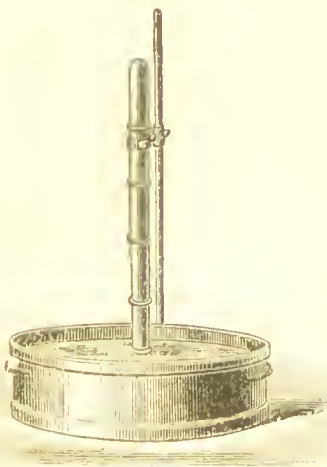
bottle of this gas when you exposed it to the air in bringing the taper into it ; nitrogen dioxide is very soluble in water, so that as fast as it was produced in the last experiment, it was dissolved. If then you add this gas nitric oxide to a measured quantity of a mixture of oxygen and nitrogen, these ruddy fumes will be produced ; if you now shake up with water, the fumes will be dissolved, and a contraction in the bulk of the gases will ensue ; by measuring this contraction you may determine how much oxygen was present in the original mixture.

On this principle analyses of air were formerly made. To illustrate the method of carrying out such analyses we will try—

Experiment V.—Take a glass tube about 30 cm. long and 2 cm. in diameter, divide it into five equal parts, each part corresponding to the contents of a smaller tube 1 cm. diameter and 14 cm. long ; mark the divisions on the outside of the large tube by slipping over it small india-rubber slippings. Pour water into the large tube, so that when inverted over the trough the water shall reach to the first ring (see fig. 14); set the tube on the beehive shelf, and fill the smaller tube, over the trough, with nitric oxide ; pass this into the larger tube, again fill the smaller tube with nitric oxide, and again pass this into the larger, in which you now have five volumes of air and two volumes of nitric oxide ; shake this tube briskly ; the oxygen of the air forms with the nitric oxide, nitrogen dioxide, which is dissolved in the water.

Add a few more bubbles of nitric oxide ; if no red fumes

FIG. 14.



are formed, the reaction is ended; again shake the tube and depress it so that the water inside and outside the tube may be at the same level; you find that the air or gas in the tube now occupies only four volumes—one volume of oxygen has therefore been taken away. Hence you conclude that five volumes of air contain one volume of oxygen.

Pour the liquid remaining in the flask used in preparing the nitric oxide into a porcelain basin, evaporate it nearly to dryness in a draught chamber, and set it aside. After some time you notice a blue solid substance formed in the basin—this is copper nitrate, produced by the action of the nitric acid on the copper: it was kept in solution by the excess of dilute nitric acid which you have evaporated off.

From these experiments you learn—

- (1) What is the method of preparing nitric oxide.
- (2) What is the behaviour of this gas towards combustible bodies.
- (3) That a high temperature is required to decompose this gas.
- (4) That with oxygen, nitric oxide forms a brown-coloured gas—nitrogen dioxide—very soluble in water.
- (5) That the formation of this nitrogen dioxide by adding nitric oxide to oxygen in a systematic manner may be made available for the analysis of air.

LESSON VIII.

PREPARATION AND PROPERTIES OF AMMONIA.

IN this lesson you have to deal with a gas which is so soluble in water that it cannot be collected over the trough. It differs much in weight from air; we can therefore use, so

to speak, an air trough in collecting the gas. This trough is the atmosphere around us ; a gas bottle is already filled and standing in this trough ; but as the gas to be collected is lighter than air, the bottle must be inverted, so that when the gas passes upwards into it the heavier air may be driven out at the mouth which opens downwards.

Mix a few grams of ammonium chloride with about an equal amount of lime, heat this mixture gently in a dry test-tube ; you recognise the well-known smell of ammonia. Repeat this experiment, using a little caustic soda instead of lime ; the same effect is produced. Moisten a small piece of red litmus paper (reddened by holding it for a moment in the fumes coming from a bottle of nitric acid), and hold it over the test-tube, it is changed to blue again ; warm it gently, the blue colour disappears.

Weigh out 10 grams of ammonium chloride (sal ammoniac), and powder it in a mortar ; also weigh out 20 grams of powdered quicklime.

Choose a flask of the same shape as that used in Lesson I. and a cork to fit it, and bore in the latter a neat round hole ; take a piece of glass tubing about 30 cm. long, bend it at right angles, the length of the smaller limb being 5 cm. ; at a distance of 10 cm. from this bend make another in the same direction, and let the third limb of the tube be 15 cm. long. The smaller limb of this tube is fitted into the cork of the flask.

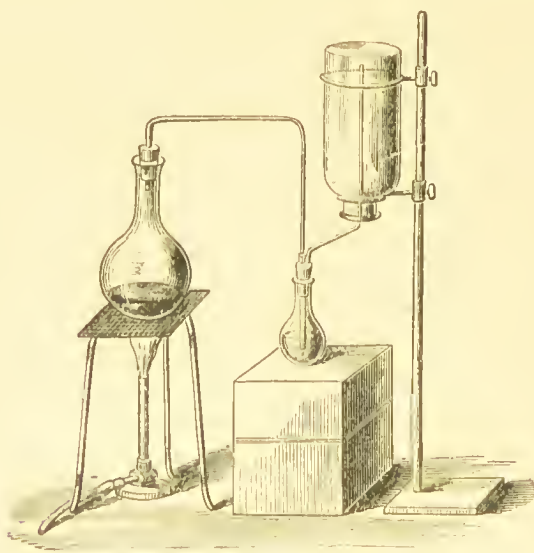
Into a small wide-mouthed bottle fit a good cork having two holes bored in it, through one of which passes a piece of tolerably wide tubing (4 or 5 cm. long), within which the longer limb of the first tube passes nearly to the bottom of the small bottle. The shorter limb of a third tube, similar to the first, except that the bends are in opposite directions, is fitted into the second hole in the cork of the small bottle, into which you now pour about 20 c.c. of ordinary ammonia solution.

Mix the sal ammoniac with two-thirds of the total quantity of the lime in a mortar, transfer the mixture to the

flask, and then add the remainder of the lime; fit the cork into the flask, and put the pieces of apparatus together, the flask standing over wire gauze on a tripod or retort-stand, while the small bottle is supported on a block of wood. A perfectly dry gas bottle is supported, mouth downwards, on another retort-stand, so that the tube leading from the small bottle may pass nearly to the top of it. The apparatus is shown in fig. 15.

By the application of a gentle heat to the flask, the sal

FIG. 15.



ammoniac and quick lime are caused to react on one another, with the production (1) of ammonia—the first portions of which are dissolved by the water in the small bottle (this at first not being quite saturated), and which is afterwards collected in the gas bottle; (2) of water—which is absorbed by the upper layer of quick lime; and (3) of calcium chloride—a white solid which remains in the flask mixed with a little undecomposed quick lime and sal ammoniac, $\text{CaO} + 2\text{NH}_4\text{Cl} = \text{CaCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$.

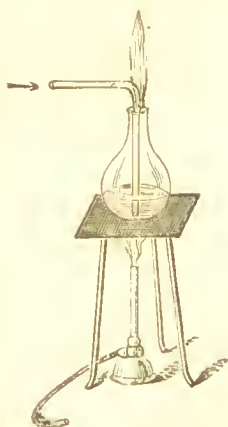
The liquid in the small bottle serves to wash the gas. The ammonia passes upwards into the gas bottle, and gathering near the top, gradually drives out the air, until at last the bottle is filled with ammonia ; when this is done, the gas will of course flow over the edges of the mouth of the bottle. You may ascertain that this is taking place by holding a piece of moistened turmeric paper close to the outside of the bottle, a little above the mouth ; it will be turned brown, showing the presence of ammonia. Now remove the bottle from the retort-stand, and set it mouth downwards on a glass plate. Fill in this way three bottles with the gas.

Experiment I.—Pass a lighted taper into one of the bottles of ammonia, supported, mouth downwards, on a retort-stand ; you notice a momentary flash of greenish-coloured flame round the taper, which is then immediately extinguished. Ammonia tends to burn when a flame is brought near it.

By mixing the ammonia with oxygen and applying a light to the mixed gases, they will burn briskly.

Experiment II.—Place about 50 c.c. of the strongest solution of ammonia in a small flask over a lamp (fig. 16) and gently heat the solution. Now pass a current of oxygen through the liquid and bring a light to the mouth of the flask ; the ammonia gas will ignite and burn with a peculiar greenish-yellow flame.

FIG. 16.

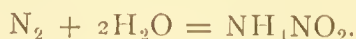


Experiment III.—Pour 30 or 40 c.c. of strong ammonia solution into a flat-bottomed flask capable of holding half a litre : wind a piece of thick platinum wire, about 30 c.m. long, round a glass tube so as to form a spiral, and arrange this on a glass rod so that it shall hang into the flask to within a centimetre or so of the ammonia solution. Make

the end of this spiral red-hot in the flame of a Bunsen lamp, and then plunge it into the flask. You see that it continues to glow, while the flask gradually becomes filled with white fumes.

In the last experiment you caused ammonia to combine rapidly with oxygen ; in this a similar combination takes place, but much more slowly. Under the influence of the heated platinum, the oxygen of the air combines with the ammonia, forming *nitrous acid*, which in turn reacts on the excess of ammonia and combines with it to form the salt *ammonium nitrite*, which you see appearing as white fumes in the flask.

This salt, ammonium nitrite, NH_4NO_2 , was formerly supposed to be formed by the evaporation of pure water in the air.



But later observations have made it very probable that pure nitrogen does not combine directly with water to form this body. Under certain conditions, however, ammonia rapidly combines with hydrogen dioxide, H_2O_2 , to produce ammonium nitrite. In this manner this salt is, in all probability, actually formed in nature, and doubtless plays an important part in the alimentation of plants. It has been shown that mainly through the medium of such compounds of nitrogen as nitric and nitrous acids and ammonia are plants able to get the nitrogen which they need for their sustenance. Experiments have proved that only a few plants have the power of assimilating the free nitrogen of the air.

The next experiment will show you the formation, in a somewhat similar manner, of another ammonium salt.

Experiment IV.—Take 3 or 4 c.c. of conc. hydrochloric acid, pour it into a small flask, set this on wire gauze on a tripod, and heat the solution. While the fumes of hydrochloric acid are coming off, bring the second bottle of ammonia, mouth downwards, over the flask ; it is immediately

filled with dense white fumes. The hydrochloric acid combines with the ammonia, forming a new substance, ammonium chloride; the product of such a union of an acid with a base is, as you already know, called a salt.

Experiment V.—Lift the remaining bottle of ammonia, mouth downwards, standing on a glass plate, into the trough filled with water, withdraw the plate and shake the bottle; the water will quickly rise until it nearly fills the jar, showing the great solubility of ammonia in water.

In this lesson you have learned—

- (1) That gases soluble in water may be collected by displacement, and how to collect such gases.
 - (2) By what reaction ammonia is produced.
 - (3) What is the action of this gas on vegetable colouring matters.
 - (4) That ammonia is a combustible gas, especially when supplied with a large amount of oxygen; that it also may be made to undergo slow combustion.
 - (5) That ammonia is very soluble in water.
 - (6) That ammonia gas is much lighter than air.
 - (7) That ammonia readily combines with certain acids, producing thereby salts of these acids.
-

LESSON IX.

PREPARATION AND PROPERTIES OF CARBON DIOXIDE.

FIT a flat-bottomed flask with a cork, through which pass a funnel tube and a delivery tube, the latter being bent twice at right angles, so that the shorter limb may be about 8 cm., and the longer 20 cm. in length. Weigh out 30 grams of marble; break it up into pieces the size of a pea, and

FIG. 17.



place these in the flask (remembering the precautions given in Lesson II.), fit the cork with the tubes in its place, and set the flask so that the longer limb of the delivery tube may dip nearly to the bottom of a gas bottle standing on a block of wood, and having its mouth covered with a piece of paste-board through a hole in which the tube passes (fig. 17). Pour a little water into the flask, and then some strong hydrochloric acid; a brisk effervescence ensues, a gas being evolved. If after the expiry of a few moments you plunge a lighted taper into the gas bottle, you will find that as it approaches the bottom of the bottle it goes out; there is evidently some

gas collecting there, and as it gathers at the bottom of the bottle, it must be a heavy gas. The molecular weight of carbon dioxide is 44 ; the gas is therefore 22 times heavier than hydrogen. But hydrogen is 14.47 times lighter than air, carbon dioxide is therefore about $1\frac{1}{2}$ times heavier than air.

Continue the evolution of gas for some time, and again bring the lighted taper into the jar ; as soon as the flame comes within the jar it is extinguished ; you have thus filled the bottle with a gas heavier than air by *downward displacement*. Fill three bottles and a small flask capable of holding about 100 c.c. with the carbon dioxide, cover them with well-greased glass plates, and set them aside.

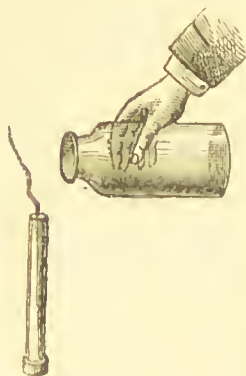
Experiment I.—Pour a little clear lime-water into a small beaker, dip the end of the delivery tube into this liquid, and allow the carbon dioxide to bubble through it ; you very soon perceive that the clear solution becomes turbid—the reason for this has been explained in Lesson I. Continue the passage of the gas, the turbidity after a time disappears. When this occurs, withdraw the delivery tube, and boil the liquid in the beaker ; the turbidity soon again makes its appearance. The disappearance of the turbidity on the continued passage of the gas is owing to the solution of the calcium carbonate in the carbonic acid ; on boiling, the solution is decomposed, carbon dioxide is evolved, and the insoluble calcium carbonate is reprecipitated.

Experiment II.—Pour a little blue litmus solution into a small flask, and pass the carbon dioxide through this liquid. You notice that it becomes a wine-red colour, differing entirely from the pure red produced by the action of nitric or hydrochloric acid upon litmus solution. Boil the reddened liquid, it becomes blue again. Now set aside, for further use, the flask employed in the preparation of the gas.

Experiment III.—Place on the table a little piece of lighted taper stuck into a cork, withdraw the glass plate from the mouth of one of the bottles of carbon dioxide, and

gradually invert the bottle as if you were pouring from it on to the taper (fig. 18). The lighted taper soon goes out.

FIG. 18.



This experiment confirms what you have already learned while preparing this gas, viz. that it extinguishes flame, and that it is heavier than air.

Experiment IV.—Put a small newly-cut piece of sodium, about the size of a pea, into the flask containing carbon dioxide, and gently heat the flask—the sodium melts, and then takes fire; cover the mouth of the flask with the thumb, and agitate it, so as to move the burning sodium about from place to place. When the sodium has ceased to burn, allow the flask to cool, and then pour a little water into it; you notice black soot-like flakes floating about in the water. The carbon dioxide has been broken up into its elements by the burning sodium, which has seized upon the oxygen so greedily as to cause evolution of light and heat, while the carbon has been liberated in the free state. Carbon dioxide, in respect of its power of supporting combustion, may be classed with nitric oxide.

Experiment V.—Pour a little water into the second bottle of carbon dioxide, close the mouth of it with the hand, and shake briskly; bring the bottle, inverted, under the water of the trough, and withdraw the hand: the water rises in the jar. Now place the hand as before, and lift the bottle out of the water; pour into it a few drops of clear lime-water, and shake several times; you notice that the liquid becomes turbid, which, as you know, is proof of the presence of carbon dioxide. You have therefore dissolved this gas in water.

Experiment VI.—Into the third bottle of carbon dioxide pour a little caustic potash or caustic soda solution, close the mouth of the bottle with the hand, and shake briskly;

bring now the bottle, inverted, under the water in the trough, and withdraw the hand. By the fact that the water rushes into the jar, you learn that the gas has been absorbed by the caustic potash.

Pour the liquid in the generating flask into a porcelain basin, and evaporate it over a flame to complete dryness, stirring the mass from time to time with a glass rod, so as to have all parts equally heated; do not allow it to gather into a hard cake, else you will have difficulty in getting it out of the basin. Put this solid substance, when quite dry, into a wide-mouthed stoppered bottle, labelling it 'calcium chloride.' This calcium chloride is the second product of the action of hydrochloric acid on marble (calcium carbonate):



You have learned then—

- (1) How to collect a heavy gas by *downward displacement*.
 - (2) That marble, when acted upon by an acid, gives off the gas carbon dioxide, CO_2 .
 - (3) That this carbon dioxide is a heavy gas.
 - (4) That it extinguishes flame.
 - (5) But that certain substances can, at high temperatures, decompose this gas, taking its oxygen to themselves.
 - (6) What is the action of carbon dioxide on lime-water and on litmus solution.
 - (7) That carbon dioxide is soluble in water, and how to recognise it in this solution.
 - (8) That this gas is absorbed by caustic potash or soda solution.
-

LESSON X.

PREPARATION AND PROPERTIES OF CARBON MONOXIDE.

PUT a few crystals of oxalic acid into a dry test-tube, drench them with strong sulphuric acid, and heat gently over a flame: you notice an effervescence in the tube; continue heating for a few moments, then bring a lighted taper to the mouth of the tube: a pale lavender-blue flame appears for an instant, passes down the tube, and goes out. Pour a little clear lime-water into another test-tube, and decant the gas (see Lesson V.) from the first tube (heating this all the while) into the lime-water; this soon becomes turbid: carbon dioxide is therefore present. But carbon dioxide is not an inflammable gas; we have therefore two gases produced in this reaction: one of them is carbon dioxide, the other carbon monoxide. Arrange the apparatus in which you prepared hydrogen (Lesson II.), setting the flask on a retort-stand. Place 10 grams of crystallised oxalic acid in the flask, and add, through the funnel tube, about 15 grams of strong sulphuric acid; heat the flask gently, and after the gas has been coming off for a few minutes, begin to collect it over the trough. Fill a bottle with the mixed gases, and set it aside, mouth downwards on a small tray. (Set the generating flask *at once* in the draught chamber, *carbon monoxide being a very poisonous gas.*)

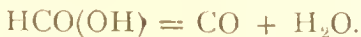
Experiment I.—Pour about 20 c.c. of a conc. solution of caustic potash rapidly into the bottle, close its mouth with the hand, and shake briskly several times. You feel by the pressure of the outside atmosphere on the hand that some gas has been absorbed by the potash within the bottle. You have already seen that carbon dioxide is produced by the action of conc. sulphuric acid upon oxalic acid; the caustic potash absorbs all this carbon dioxide, leaving the monoxide untouched. Now invert the bottle beneath the water in the

trough, and withdraw the hand ; the water rushes in until it fills about one half of the bottle.

Sulphuric acid heated with oxalic acid gives rise therefore to equal volumes of carbon monoxide and dioxide. The sulphuric acid acts by taking away the elements of water, $C_2H_2O_4 - H_2O = CO_2 + CO$.

Experiment II.—Decant the gas remaining in the bottle used in the last experiment into another smaller bottle, and bring a light to its mouth ; the gas burns with the peculiar pale blue flame noticed in the preliminary experiments. When the flame has gone out, add a little lime-water to the bottle, and shake it briskly. A turbidity tells you that carbon dioxide is present. By burning carbon monoxide, therefore, carbon dioxide is produced. This is in keeping with what you have already learned about combustion. The monoxide, CO, has been burned or oxidised, a compound relatively richer in oxygen being produced.

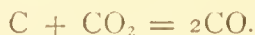
There is another method of producing this carbon monoxide which is one of much interest. Take about 10 grams of formic acid, and add to this, in the apparatus you have just used, 15 grams of strong sulphuric acid. Gently heat the flask, and collect over the trough a bottle full of the gas which is evolved. Test this gas, first by shaking it with caustic potash—nothing is absorbed ; then apply a light, when you at once see, by the colour of the flame, that the burning gas is carbon monoxide. By the action of sulphuric acid upon formic acid, pure carbon monoxide is produced. Formic acid, H_2CO_2 , gives up to sulphuric acid the elements of water, H_2O , while carbon monoxide, CO, remains.



Formic acid may be prepared by heating together for several hours glycerin, oxalic acid, and a little water, then adding more water, and raising the temperature : liquid formic acid distils over. The same amount of glycerin may be again used to effect the transformation of a fresh quantity

of oxalic acid. Formic acid was formerly obtained from ants, or from certain plants, *e.g.* nettles—in which it exists; sometimes also by the reaction mentioned above; but in this case the oxalic acid was itself obtained from plants, so that formic acid was entirely of animal or vegetable origin. But the experiment you have just performed, *viz.*, splitting this acid into carbon monoxide and water, suggested the idea that by combining these two substances together formic acid might be re-formed. This has actually been done, and the chemist has thus built up from *inorganic* or *mineral* constituents a substance formerly obtainable only from organised forms. Such a building up is termed *synthesis*, and is exactly opposed to *analysis*, or pulling to pieces.

You may have noticed on a winter's evening a pale blue flame playing on the surface of a coal fire, when the coals were red-hot and little or no smoke was emitted from them. This flame was produced by burning carbon monoxide. You have already learned (in Lesson I.) that by burning carbon, carbon dioxide is produced; by burning coals, therefore, this gas is formed; but this carbon dioxide in passing through the layer of red-hot coals in the upper part of the fire is robbed of part of its oxygen, carbon monoxide being produced, while the oxygen unites with another atom of carbon to form the same gas, carbon monoxide; thus carbon monoxide is the ultimate form assumed by the gas produced in the combustion of coal in such a fire as that described.



From the experiments in this lesson you learn—

- (1) What is the action of sulphuric acid upon oxalic acid.
- (2) That carbon monoxide is a combustible gas, producing, when burned, carbon dioxide.
- (3) That carbon dioxide can be separated from the monoxide by shaking the mixed gases with caustic potash solution.

- (4) That carbon monoxide is produced in a coal fire.
- (5) What is the action of sulphuric acid on formic acid.
- (6) What is the meaning of the term synthesis.

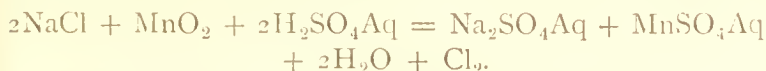
LESSON XI.

PREPARATION AND PROPERTIES OF CHLORINE.

HEAT a little manganese dioxide with a little conc. hydrochloric acid in a test-tube ; a yellowish-green gas * with an extremely pungent odour is evolved :



A more uniform stream of chlorine gas is obtained by acting on a mixture of manganese dioxide and sodium chloride with dilute sulphuric acid :



Weigh out about 30 grams of manganese dioxide and the same amount of sodium chloride, mix them in a mortar, and transfer the mixture to a large flat-bottomed flask. Mix cautiously 38 grams of water with 60 grams of conc. sulphuric acid in a large beaker, and allow this mixture to cool. The apparatus is similar to that in which you prepared carbon dioxide (Lesson IX.), but the generating flask must be considerably larger, and a caoutchouc cork should be used. You know that chlorine has the atomic weight 35.5 ; it is therefore $35\frac{1}{2}$ times heavier than hydrogen, but hydrogen is $14\frac{1}{2}$ times lighter than air. How therefore must chlorine be collected : by upward or downward displacement ? When you have settled the arrangement of the receiving

* Hence the name *chlorine*, from $\chi\lambda\omega\rho\delta\varsigma$ = yellowish green.

bottles, pour the cold mixture of sulphuric acid and water through the funnel tube into the flask ; an action at once ensues, the flask gradually becomes filled with yellowish-green vapours, which pass over into the receiving bottle. *Conduct all operations with chlorine in a draught chamber, as the fumes of this gas are very hurtful.* Make sure that all the connections in the apparatus are tight. (Should you get a whiff of the gas into the lungs, pour a little alcohol on to a piece of filtering paper, and hold this over the mouth and nose so as to inhale the vapours.) When judging by the colour, you think that the bottle is full of chlorine, remove it, cover it with *a well greased* glass plate, and set another in its place. Fill thus seven bottles, and proceed to test the properties of the gas.

Should the flow of gas slacken, apply a gentle heat to the generating flask by means of a small Bunsen lamp ; the action will soon go on briskly again.

Experiment I.—Invert the first bottle of chlorine in the trough, withdraw the plate, and shake the bottle ; the water gradually rises in the jar, showing you that this gas is very soluble in water. It is this property of chlorine that obliges us to have recourse to collection by displacement.

Experiment II.—Moisten a piece of madder-dyed red cloth with water, and put it into one of the bottles of chlorine ; cover the mouth of the bottle with a glass plate, well greased where it touches the bottle, and notice how the red colour of the cloth gradually disappears ; allow the bleaching action to go on, and proceed with—

Experiment III.—Quickly pour a little conc. sulphuric acid into the third bottle of chlorine, replace the glass plate, and shake the bottle several times ; after a little time introduce into the bottle a *dry* piece of dyed cloth, similar to that used in last experiment. It is not bleached. The sulphuric acid, by taking away all moisture present in the jar, dries the chlorine, and this gas, when perfectly dry, does not bleach.

Experiment IV.—Moisten a strip of filtering paper with turpentine, and plunge it into the third bottle of chlorine ; a cloud of black smoke is at once produced, accompanied by a momentary flame, and you find the paper charred and blackened in the jar. The affinity which chlorine possesses for hydrogen is very great, and as turpentine is a compound of carbon and hydrogen, the hydrogen is seized upon by the chlorine, and separated from the carbon or charcoal, which, as you know, is a black soot-like substance. With another bottle of chlorine you may perform an experiment showing the great readiness wherewith chlorine combines with metals.

Experiment V.—Place a little powdered metallic antimony on a small piece of paper, and from this shake it slowly into the bottle containing chlorine. The antimony, as it falls, burns, each little grain sparkling brilliantly. Chlorine and antimony have therefore very great readiness to combine with one another, and much light is produced by the intensity of their combination.

Experiment VI.—Into another bottle of chlorine plunge a piece of phosphorus supported on the deflagrating spoon ; the phosphorus takes fire and burns with a brilliant flame, showing you that chlorine very eagerly combines with this substance as well as with so many others.

Experiment VII.—Put two pieces of paper into the last bottle of chlorine with some letters printed or written on each, those on one paper being printed with common ink, those on the other with printers' ink.

You notice that the common ink is soon bleached and almost entirely disappears, while the letters formed with printers' ink remain unacted upon. This is a further illustration of the affinity of chlorine for hydrogen. Common ink is a vegetable substance, and contains a considerable quantity of hydrogen united with other elements ; while printers' ink is essentially a mixture of carbon, in the form of lampblack, with some thickening material.

Experiment VIII.—Place a few grains of powdered iron pyrites in a test-tube with a little water, and, while you shake the tube so as to keep the solid particles suspended in the water, pass a gentle stream of chlorine through the liquid. (The materials used in preparing chlorine for the foregoing experiments will probably, if heated, yield enough of the gas for this experiment.) The pyrites rapidly disappears, and you have soon only a few fine white particles floating about ; allow these to settle, pour the clear liquid into another test-tube, divide it into two portions, and apply a chemical test to each.

To portion (1) add a little barium chloride ; a dense white precipitate immediately forms. This, as you will hereafter more fully learn, is proof of the presence of *sulphuric acid*, or a *sulphate*.

To portion (2) add a little ammonia ; a foxy-red precipitate tells you that iron, in a high state of oxidation, is present.

Iron pyrites is essentially sulphide of iron. The action of the chlorine has been to combine with the hydrogen of the water, while the oxygen thus liberated has attacked the iron and sulphur and oxidised them.

You thus see how chlorine may be made an exceedingly valuable *oxidising* agent.

From these experiments then you learn—

- (1) How to prepare chlorine.
 - (2) That this gas is very soluble in water.
 - (3) That chlorine very readily combines with many substances, especially with hydrogen.
 - (4) That this property may be applied to bleaching purposes.
 - (5) That chlorine may be made to act as an oxidising agent.
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LESSON XII.

PREPARATION AND PROPERTIES OF HYDROCHLORIC ACID.

PLACE a few grains of common salt in a test-tube, and add a drop or two of conc. sulphuric acid ; a brisk effervescence ensues, and a gas having a strongly acid pungent odour is given off. The semi-fluid mass in the test-tube solidifies on cooling, forming hydrogen sodium sulphate. This reaction is exactly analogous to that by which you prepared nitric acid, NO_3 being in this instance replaced by Cl , and K by Na :



Into the flask used in preparing carbon dioxide (see Lesson IX.) put about 20 grams of common salt in lumps. To get the salt into this state, fuse it in an iron ladle in the furnace, and when cool break it up into pieces. Pour, through the funnel tube, conc. sulphuric acid sufficient to cover the salt in the flask, which is set on a retort-stand, and place a bottle to collect the gas, as in the case of carbon dioxide, testing when the bottle is full by bringing a lighted taper near the mouth of the bottle ; if the light is extinguished, remove the bottle, and cover it with a greased glass plate. Fill thus two bottles with the gas. If the action slackens, apply a gentle heat.

You have already noticed, while testing if the bottles were full of gas, that hydrochloric acid is incombustible, and that it does not support combustion.

Experiment I.—Bring a piece of blue litmus paper into the first bottle of the gas, the paper is at once reddened ; this property of reddening litmus you already know to be a property of acids.

Experiment II.—Bring the other bottle, inverted, beneath the water in the trough, withdraw the plate and shake the bottle briskly ; it is rapidly filled by the water rising within

it. This experiment shows you the great solubility of hydrochloric acid in water. Ordinary hydrochloric acid consists of a solution of the gas in water. That the gas is to a certain extent expelled from such a solution, on boiling, you have already had proof (Lesson VIII., Experiment IV.)

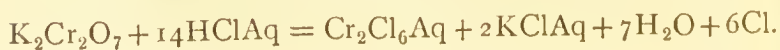
Experiment III.—To prepare such a solution, fit up an apparatus similar to that used in making the ammonia solution, but in the small bottle put a little ordinary dilute hydrochloric acid, and let the delivery tube from this bottle dip downwards into a receiving bottle, which is partially filled with water.

The fumes formed when hydrochloric acid gas issues into the air are caused by the condensation of the gas by the moisture in the atmosphere.

The neutralisation of this acid by ammonia and consequent production of the salt ammonium chloride, you have also already noticed.

Experiment IV.—Fill a bottle with hydrogen, and another over the trough, using *warm* water, with chlorine; pass equal volumes of each of these into a soda-water bottle, cork it, surround it with a cloth, and shake it well; withdraw the cork and bring a light to the mouth of the bottle; a loud explosion ensues, and the formation of hydrochloric acid is rendered evident by the white fumes which appear on bringing a little ammonia to the mouth of the soda-water bottle. Hydrochloric acid gas therefore seems to be composed of equal volumes of hydrogen and chlorine.

Experiment V.—Heat, in a test-tube, a little conc. hydrochloric acid with a few crystals of potassium dichromate; by the colour and smell of the issuing gas you at once recognise it to be chlorine. As in Experiment IV. you built up hydrochloric acid from hydrogen and chlorine, so in this experiment you have broken up the acid, liberating its constituent elements:



In this lesson you learn—

- (1) Some methods by which hydrochloric acid can be prepared.
 - (2) That this gas is soluble in water, and the practical application of this fact.
 - (3) What is the action of hydrochloric acid upon litmus.
 - (4) That fumes are caused when hydrochloric acid gas issues into the air, and the reason of this.
 - (5) What is the synthetical method of preparing this gas, and what we thus learn of its formation.
 - (6) One of the analytical methods of breaking up hydrochloric acid.
-

LESSON XIII.

PREPARATION AND PROPERTIES OF OXYGEN DERIVATIVES OF CHLORINE.

FIT up an apparatus for generating chlorine, using half as much salt, manganese, &c., as directed in Lesson XI. Make about 200 c.c. of a tolerably conc. solution of caustic potash, place this in a beaker which is kept cool by being surrounded with water, and lead the chlorine gas which is generated into the liquid. After a few minutes remove the beaker, pour about half of its contents into another dish, place the beaker, resting on wire gauze, on a stand with a lamp beneath, and continue to pass in the chlorine gas, keeping the solution boiling. Meanwhile make a few experiments with that part of the solution which you have set aside.

First notice its smell : it is sensibly different from that of chlorine, although chlorous.

Experiment I.—Dip a piece of madder-dyed cloth into the solution : the cloth is not bleached.

Experiment II.—To a small quantity of the solution in a test-tube add a drop or two of hydrochloric acid. Action ensues, and a gas is given off which, by its smell and colour, you at once recognise to be chlorine.

Experiment III.—Again dip the piece of cloth used in Experiment I. into the solution, then pass it quickly through dilute hydrochloric acid, and afterwards wash it in water ; it is now bleached. You see that, by the action of the acid on the solution contained in the pores of the cloth, chlorine is liberated ; as the cloth is moist, it is bleached by this chlorine.

The solution you have just been experimenting with is a mixture of potassium hypochlorite and chloride : $2\text{KHO}\text{Aq} + \text{Cl}_2 = \text{KClO}\text{Aq} + \text{KCl}\text{Aq} + \text{H}_2\text{O}$. Solution of bleaching powder contains the corresponding calcium compounds. To illustrate its formation, perform —

Experiment IV.—Fill a dry flask with chlorine by downward displacement, put into it a little powdered quicklime, and shake the flask ; the yellow gas gradually disappears, being absorbed by the lime (as it was by the caustic potash). Pour a little water into the flask, and shake it up with the bleaching powder which you have made ; then test the bleaching effect of the solution, as in Experiment III.

You now understand the object of dipping the goods into acid (*souring*, as it is termed) after passing them through the bleaching powder solution.

To the remainder of the solution of potassium hypochlorite add a little very dilute nitric acid, place the mixture in a retort to which a small receiver is adapted, and apply a gentle heat. After a little time a colourless peculiarly smelling liquid condenses in the receiver. This is a solution of hypochlorous acid, HClOAq .

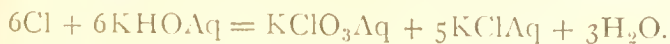
Experiment V.—Dip a piece of dyed cloth into the distillate you have just obtained ; the colour of the cloth is at once discharged.

Experiment VI.—Add a few drops of dilute hydrochloric

acid to another portion of the liquid ; chlorine is generated. You can now more fully understand the action of bleaching powder. When the goods are soured, the first effect of the acid probably is to produce hypochlorous acid—just as you have done ; but this (as you have shown in Experiment VI.) is at once decomposed, chlorine being liberated.

You may now put together all you have learned about chlorine, and attempt to answer the question, *How does chlorine bleach?* If you consider that dry chlorine gas alone does not discharge vegetable colouring matters (Lesson XI., Experiment III.) ; that chlorine very readily combines with hydrogen (Lesson XI., Experiment IV.) ; that chlorine in presence of moisture does bleach (Lesson XI., Experiment II.) ; and that moisture or water consists of hydrogen and oxygen (Lesson III., Experiment I.)—you will be led to the conclusion that the bleaching action of chlorine must depend upon its power of combining with the hydrogen of the water present, and thus liberating oxygen. When a chemical reaction is accomplished wherein oxygen is produced, the oxygen sometimes interacts with other constituents of the system, and oxidised compounds are thus formed. In the present case oxidised compounds are formed, and these are removed in the subsequent washing.

Return to the heated potash solution through which you have been passing chlorine ; it will now be saturated with the gas. Remove the chlorine-generating apparatus, pour the solution into a basin, evaporate it to about half its bulk, and set it aside. A salt crystallises out on cooling ; drain off the liquid, and dry the crystals between folds of filtering paper. These are crystals of potassium chlorate,



Most of the potassium chloride formed remains in solution, as this salt is more soluble than the chlorate. You have thus roughly separated two salts by taking advantage of their different degrees of solubility in water.

Experiment VII.—Take one or two of the crystals you have prepared, place them in a test glass, cover them with water, put into the glass a very small piece of phosphorus, and set a funnel tube in the glass so that its lower extremity just touches the crystals (see fig. 19), pour a few drops of conc. sulphuric acid down the funnel tube; a greenish gas is evolved which, coming in contact with the phosphorus, attacks it so violently as to cause it to take fire even under water. This gas is another oxide of chlorine, viz. the tetroxide, Cl_2O_4 . You have here an instance of very intense chemical action.

FIG. 19.



In this lesson you learn :—

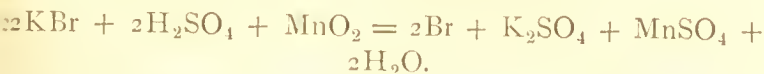
- (1) The modes of producing some of the oxygen derivatives of chlorine, and their leading properties.
- (2) One of the methods for separating two salts occurring together in solution.
- (3) The *modus operandi* of bleaching, and the way in which chlorine bleaches.

LESSON XIV.

PREPARATION AND PROPERTIES OF BROMINE.

INTO a small stoppered retort pour a mixture of 3 grams of manganese dioxide with $1\frac{1}{2}$ grams of potassium bromide, set the retort on wire gauze on the ring of a stand, allowing its beak to pass into a small receiving flask, which is kept cool by being surrounded with cold water. Take out the stopper of the retort and pour in about 20 c.c. of conc. sulphuric acid, replace the stopper and gently heat the retort. Dark-

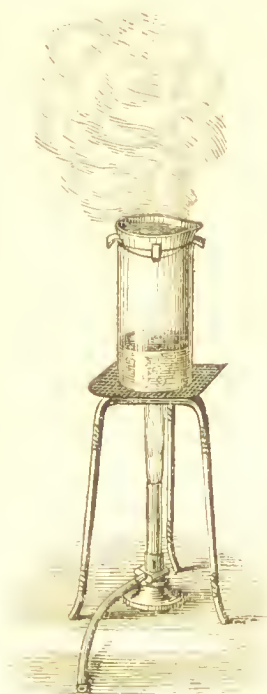
red fumes speedily fill the apparatus, and a heavy dark-red liquid condenses in the receiver ; when you have collected a few cubic centimetres of this liquid, remove the lamp. (Conduct the operation in a draught chamber.) Bromine is produced in this reaction in a manner exactly analogous to the reaction employed in preparing chlorine.



Compounds of bromine with sodium, magnesium, or potassium occur in sea water. To illustrate the preparation of potassium bromide, from which bromine itself can, by the above reaction, be prepared, you may perform the following experiments:—

Experiment I.—Dissolve a few crystals of potassium bromide in water in a test-tube, add a little chlorine water to the solution, and shake the tube ; the bromine is displaced from its combination with potassium by the chlorine, and is dissolved in the water ; hence the yellowish-red colour now observed. Add now a few cubic centimetres of ether and shake the tube ; all the bromine is concentrated in the ethereal solution which floats on the surface ; draw this off by means of a little pipette, and add to it caustic potash until the red colour nearly disappears ; evaporate the solution on a small water-bath, formed by placing a basin on the top of a beaker containing a little water—a piece of filtering paper between the basin and the beaker separates these

FIG. 20.



so that the steam may escape—(fig. 20), and when dry, strongly heat the residue over a Bunsen flame. You have now pure potassium bromide, from which, as you know, bromine is easily prepared.

You have already detected the very irritating odour of bromine (whence its name, *βρωμος* = a bad smell).

Experiment II.—Add to a few drops of bromine about thirty times their volume of water, and shake the mixture; you thus obtain a clear yellowish-red solution. Dip a piece of madder-dyed cloth into this solution: it is slowly bleached, the action being less intense than in the case of chlorine.

Experiment III.—Pour a few drops of bromine into a wide-mouthed bottle, and heat it gently until the bottle is full of bromine vapours; cut and dry a small piece of phosphorus, place this on the deflagrating spoon and plunge it into the bottle; the phosphorus combines with the bromine so energetically that light is evolved. Chlorine also, you remember, similarly combined with phosphorus.

The reaction of bromine with phosphorus is typical of that which occurs between bromine and many other substances.

From these experiments you learn—

- (1) By what method bromine is prepared.
- (2) That bromine is slightly soluble in water.
- (3) That this solution possesses a certain bleaching action.
- (4) That the vapour of bromine is intensely irritating.
- (5) That bromine has a very energetic action upon many substances.

LESSON XV.

PREPARATION AND PROPERTIES OF IODINE AND
HYDRIODIC ACID.

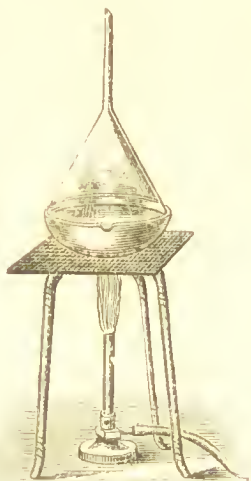
PLACE a mixture of two grams of manganese dioxide with one gram of potassium iodide in a round-bottomed flask, resting on a retort-stand ; pour about three or four cubic centimetres of conc. sulphuric acid, through a funnel tube, on to the mixture, and gently heat the flask ; you soon notice violet coloured fumes appearing which gradually fill the flask, condensing in the neck, and forming brilliant metallic-looking plates. When a sufficient quantity of iodine has been thus produced, collect a little of it, by scraping it off the flask with a glass rod or horn spatula and place it in a clean dry test-tube.

This reaction is exactly analogous to that used in last Lesson for the preparation of bromine ; you can easily formulate it for yourself.

Experiment I.—Put a few crystals of iodine in a small porcelain basin (about 4 cm. diameter), place an inverted funnel over this, resting on the basin (fig. 21), and set the whole apparatus on a piece of wire gauze on a tripod stand ; now *very gently* heat the basin ; the iodine rises in beautiful violet vapours filling the funnel, on the sides of which it again condenses, forming small glancing crystals.

If you call to mind Lesson V., in which you prepared nitric acid by a process of *distillation*, you will see that this process agrees with that then performed—only you now

FIG. 21.



distil a solid, by causing it to become a gas, which is again condensed to a solid : such a process is termed *sublimation*.

Experiment II.—Take a single crystal of iodine and shake it up with water in a test-tube ; very little is dissolved, the water however is slightly tinged yellow. To this solution add water which has been boiled with a *very small* piece of starch ; a blue colour is at once produced. Heat this solution ; the blue colour disappears, but reappears again when the solution cools. In the formation of this blue substance with starch you have then a means of easily detecting the presence of iodine.

Experiment III.—Make a solution of potassium iodide in a test-tube, and add to this a few drops of starch paste ; no blue colouration ensues. Now add one drop of chlorine water, the blue colour instantly makes its appearance ; on adding some more chlorine water the solution again becomes colourless, owing to the formation of a chloride of iodine which has no action on starch. Iodine compounds therefore alone do not give a blue colour with starch, it is only free iodine that does this. By the addition of the chlorine water the potassium iodide was decomposed, potassium chloride being formed and iodine set free, which immediately reacted on the starch. By paying attention to what you saw in performing the last experiment, you will be able to say what special precautions must be taken in applying this test to iodine compounds.

Experiment IV.—Place a *small* piece of dry phosphorus in a basin and throw into it a few crystals of iodine ; after a very few moments combination of the two substances takes place accompanied by the evolution of light and heat.

Experiment V.—Put a few crystals of iodine into a small flask and heat this until it is filled with iodine vapours ; now throw into the flask a little piece of sodium, and continue heating the flask gently ; the sodium combines with the iodine so energetically that light is evolved.

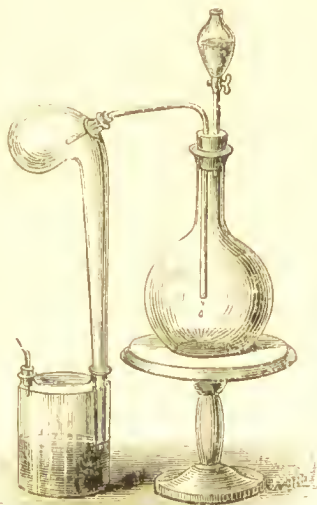
Experiment VI.—Dissolve one crystal of potassium iodide in water, add a very few drops of a solution of potassium

bromide, and then cautiously a little chlorine water; the liquid becomes yellowish-red in colour. Now add a little ether and shake the tube; the iodine, liberated from the potassium iodide by the action of chlorine, is dissolved in the ether, to which it imparts a violet colour; this ethereal solution may be drawn off by means of a pipette. A little more chlorine water is now to be added, and again a few cubic centimetres of ether; this dissolves out the bromine, which is now liberated, and which shows its presence by the distinct orange (not violet) colour imparted by it to the ether. You learn thus how iodine and bromine may be separately obtained from a liquid in which they exist together, such as the liquid produced by lixiviating kelp or the ashes of sea-plants, which again obtain their iodine and bromine from the sea itself.

For the preparation of hydriodic acid we make use of the reaction of Experiment IV. somewhat modified.

Fit up an apparatus like that represented in fig. 22, consisting of a flask fitted with a cork carrying a small separating funnel, and a tube leading into a retort the beak of which, passing through a cork into a two-necked bottle, dips about 3 cm. below the surface of the water in this bottle (this water is coloured blue with litmus). In the flask place 2 grams of amorphous phosphorus, and 15 grams of iodine; now very gently heat the flask until these combine to form a blackish-looking mass; when this is cool, fill the bulb of the separating funnel with cold water, and, by turning the stopcock, allow this to flow, *drop by drop*, on to the phosphorus tri-iodide in

FIG. 22.



the flask (this is the compound produced by the mutual action of phosphorus and iodine upon one another), which is decomposed : $\text{PI}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HI}$. Hydriodic acid, HI, is evolved, and passes into the retort, and thence into the water in the bottle, by which it is readily dissolved. This gas, being very soluble in water, is sometimes so quickly absorbed as to cause a partial vacuum in the retort, into which the water rushes ; but, before the bulb of the retort is filled with water, the level in the bottle sinks below the beak of the retort ; thus no water is allowed to flow back into the flask. The blue colour of the water you notice gradually turns to red.

Experiment VII.—Disconnect the apparatus and arrange it so that the gas shall pass into an empty dry two-necked bottle, into which, through the second neck, you lead chlorine. Violet vapours filling the bottle show the presence of free iodine ; the hydriodic acid therefore has been decomposed by the chlorine, hydrochloric acid being formed, and iodine set free. In this respect hydriodic acid differs from its chlorine analogue hydrochloric acid.

The bromine analogue hydrobromic acid, HBr, also exists and is formed by a reaction similar to that employed above.

From your experiments in this lesson you learn—

- (1) The method of preparing iodine.
- (2) The meaning of the term *sublimation* ; and that iodine may be sublimed.
- (3) The reaction of free iodine with starch.
- (4) The intense action of phosphorus upon iodine.
- (5) The application of the reaction noted in (4) to the preparation of hydriodic acid.
- (6) The solubility in water of the gas hydriodic acid, which agrees in this respect with hydrochloric acid, but differs in—
- (7) The fact that it is decomposed by chlorine, hydrochloric acid and iodine being formed.

LESSON XVI.

PREPARATION AND PROPERTIES OF HYDROFLUORIC ACID, SILICON FLUORIDE, AND HYDROFLUOSILICIC ACID.

Experiment I.—Take a small circular piece of sheet lead, about 6 or 7 cm. diameter, place this in a mortar, and, with the pestle, press the centre of the lead inwards; you thus form a little leaden cup—a platinum crucible or basin, if you have one, will do instead of this cup. Gently warm a plate of glass large enough to cover the mouth of the little dish, and rub over it a piece of beeswax, so that the plate is equally covered with a thin coating of this substance. Into the leaden dish put about 5 or 6 grams of powdered fluor-spar, and drench this with conc. sulphuric acid. Trace some device on the glass plate with a sharp-pointed piece of wood, or wire, making sure that the lines are drawn quite through the wax. Place the plate over the leaden dish with the side on which the lines are drawn downwards. Apply a gentle heat to the dish for a few moments; you notice that white fumes are evolved and fill the space between the glass plate and the dish. After a few minutes remove the glass plate, wash out the leaden cup, and remove the wax from the glass by rubbing it with a warm cloth; the design which you traced is seen to be etched into the glass. You infer therefore that, by the action of sulphuric acid upon fluor-spar, a gas has been produced which has the property of etching glass.

You at once see the reason for not using a glass vessel in the preparation of the gas.

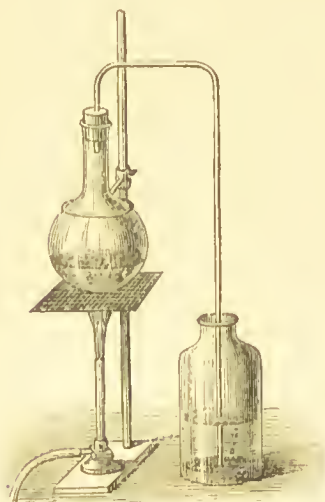
The reaction which occurs between the sulphuric acid and fluor-spar is thus formulated:



You noticed the fumes produced by the hydrofluoric acid in the air, and you have learned something about its remarkable action on glass; the following experiments will explain this action more fully.

Experiment II.—Arrange an apparatus similar to that used in the preparation of carbon dioxide, but let the flask rest on a retort-stand ; into the flask put a mixture of 10 grams of powdered fluor-spar with about 15 grams of fine white sand. Into one of the gas bottles intended for the collection of the gas pour mercury sufficient to form a layer on the bottom to the depth of 10 or 12 mm., and let the delivery tube from the flask dip beneath this mercury (fig. 23). In the first instance, however, use a dry empty bottle for the collection of the gas.

FIG. 23.



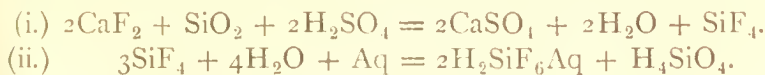
Pour, through the funnel tube, about 20 c.c. of conc. sulphuric acid. Shake the flask well, so as to mix the substances in it, and apply a gentle heat. A gas, which fumes in the air, soon begins to come off. Do not apply much heat in this process, otherwise the mixture in the flask will froth up and may come over. When a few minutes have elapsed, bring a lighted taper into the gas bottle ; if it is extinguished immediately on entering the bottle, sufficient gas has been

collected. You learn by this that the gas is heavier than air, that it is incombustible, and that it does not support combustion. Remove the bottle of gas, and in its place set the second bottle containing the mercury ; let this bottle be nearly filled with water, and allow the evolution of gas to proceed, while with that already collected you perform—

Experiment III.—Attach, by means of caoutchouc tubing, a small piece of glass tubing drawn to a tolerably fine point, to the end of a funnel tube. Pour a little water into the

funnel ; the opening of the small tube should be of such a size that the water slowly trickles out at it. Bring this tube within the bottle containing the gas ; as each drop of water falls from the opening of the narrow tube, it seems to turn solid, and after some time you have a long stalaetite hanging from the end of the tube.

Let us consider how this is brought about. Fluor-spar and sulphuric acid, as you have just learned, react to produce hydrofluoric acid ; this interacts with the sand you placed in the flask (sand is nearly pure silica), and forms the gas silicon tetrafluoride, which you have collected. This gas is decomposed by water, silica being produced. As each drop of water came into contact with the silicon tetrafluoride, the gas was decomposed, and the silica thus formed coated the drop of water, holding it as in a bag :



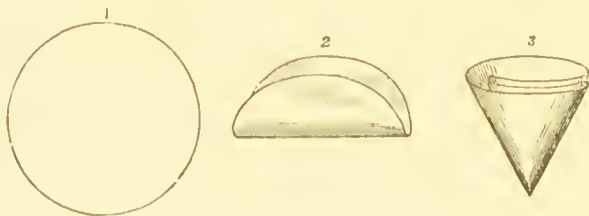
If you now look at the other bottle, you will see an action going forward similar to that which you have just noticed. As each bubble of gas comes up through the water, it is coated with silica, which gradually accumulates on the surface, until the water is full of this silica in a very finely divided state. Were it not for the layer of mercury the silica would soon choke up the mouth of the delivery tube. When the action has proceeded for some time, you may remove and wash out the generating flask. Cover the bottle with a glass plate, while you perform—

Experiment IV.—You remember the action of hydrofluoric acid upon glass ; you also know how this gas is produced ; and in the last experiment you have seen that the mutual action of silica, fluor-spar, and sulphuric acid, when heated together, is to produce the gas silicon fluoride : therefore you may infer that the way in which hydrofluoric acid etches glass (which is a compound of silicon), is by seizing upon the silica in the glass, and forming therewith this silicon

fluoride. To verify this supposition is the purpose of the present experiment. Put a little fluor-spar into the leaden dish, adding to it sulphuric acid as before ; cover the dish with a glass plate, in the centre of which you have put a drop of water, and heat gently. You soon see that the drop of water is coated with a film of silica ; therefore you conclude that the gas silicon fluoride is actually produced and is decomposed by the water.

The solution in the gas bottle (Experiment II.) is now to be separated by *filtration* from the finely divided silica suspended in it. Take a medium-sized glass funnel, and a circular piece of filtering paper (fig. 24, No. 1). (It is convenient to have your filtering paper cut in circular pieces of

FIG. 24.



various sizes, about 4, 6, 8, 10, and 12 cm. diameter.) Fold the paper so as to form a half-circle (fig. 24, No. 2), and then again at right angles to the first fold (fig. 24, No. 3). Open out the paper thus folded, and you have a filter formed—three folds of the paper being on one side, and one on the other. The funnel chosen should be rather larger than the filter. Set the filter inside the funnel, moisten the paper with a few drops of water, and with the finger press the filter to the sides of the funnel, leaving no bubbles of air between the paper and the glass. Place the funnel in the ring of a retort-stand, or on a filter-stand, a beaker glass being set below it to receive the filtered solution, or *filtrate*, as it is termed.

Now slowly pour the liquid down a glass rod held in one hand from the gas bottle on to the filter. The liquid is thus delivered directly on to the filter, and all loss from spirting avoided. The lower end of the funnel should, for the same reason, rest against the side of the beaker; the filtered liquid thus gently runs down the side of the glass (fig. 25). Carefully filter off the suspended silica from the liquid, set aside

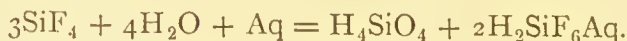
FIG. 25.



the silica on the filter for further use, and proceed to examine the solution.

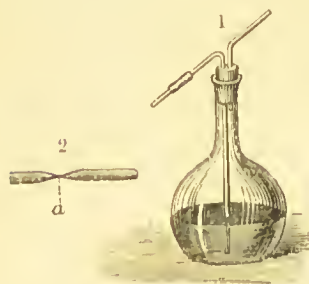
Touch a piece of blue litmus paper with a drop of the solution, on the end of a glass rod; the litmus paper is reddened: you have, probably, an acid in the solution. To a little of this acid liquid, in a test-tube, add a drop or two of barium chloride solution: a white precipitate is immediately produced. This application of *hydrofluosilicic acid* (as it is called) for the detection of barium is one which

you will have occasion to use hereafter. The action of water on silicon fluoride is to form silicic acid, and hydrofluosilicic acid :



The new acid should be kept in a gutta-percha bottle, as it gradually acts upon glass. The silica on the filter,

FIG. 26.



which you set aside, is now to be washed, dried, and preserved for subsequent use. To wash a precipitate, you require a wash-bottle (see fig. 26, No. 1).

Choose a flat-bottomed flask, capable of holding about three-quarters of a litre, also a good cork to fit this flask (preferably a caoutchouc cork); in the cork bore two holes. Fuse the edges of a piece of glass tubing about 10 cm. longer than the height of the flask, and bend this tube, at about 10 cm. from the end, so as to form an obtuse angle. Take another little piece of tubing, gently soften it in the Bunsen flame, keep turning it round, and *very gradually* drawing it out, so that you obtain a tube like that represented in fig. 26, No. 2, the glass in the narrow part being tolerably thick. Allow it to cool, and cut it at the point *a*. Fuse the edges of this tube, and attach it to the shorter end of that already made by a little piece of caoutchouc tubing. Take another piece of glass tubing, about 10 cm. long, bend it gently about the middle, and round its rough edges. Now fit these two tubes through the cork of the flask, so that the longer may dip to the bottom of, the shorter only a little way into, the flask. By blowing in at the shorter tube a stream of water is forced out at the narrow opening of the longer. By turning the small jet attached by flexible tubing, you can direct the stream of water in any direction you please. Fill the wash-bottle with water, and proceed

to wash the silica in the filter, sending the stream of water in a circular direction round the filter, so as to bring all solid matter into the centre of the filter ; when you have filled up the filter with wash water, allow it to drain through before adding more. Continue the washings until all acid is removed (that is, until the washings no longer redden litmus paper), then cover the funnel with a piece of paper, and set it aside to dry. When dry, put the silica into a stoppered bottle, and preserve it.

In this lesson you learn—

- (1) By what method hydrofluoric acid is prepared.
- (2) That this acid etches glass, and the reaction by which it does this.
- (3) By what method silicon fluoride is prepared.
- (4) That this gas is decomposed by water ; and
- (5) That hydrofluosilicic acid is thus produced.
- (6) That a solid may be separated from a liquid by filtration.
- (7) What is the use of the wash-bottle.

LESSON XVII.

PREPARATION AND PROPERTIES OF METHANE (MARSH GAS).

INTRODUCE into an iron tube about 20 cm. long and 5 cm. diameter (see fig. 27) a mixture of 8 grams of dry sodium acetate with 8 grams of caustic soda—previously strongly heated on an iron plate—and 12 grams of lime. Fit in a good cork with a delivery tube, arrange the trough and a bottle to collect the gas ; now heat the tube, beginning at the

upper part, and heating gradually downwards. As the gas does not come off until a pretty high temperature is reached, it is preferable to use such an apparatus as that described, than to heat the mixture in a glass flask, which is very liable to crack. The gas may be prepared by heating, in a small retort, 15 grams sodium acetate, that has been fused, *well mixed* with 30 grams soda lime.

FIG. 27.



The lime in the above mixture serves to render it more infusible, and to prevent it stopping up the tube. As the bubbles of gas pass through the water in the trough, test them from time to time by bringing a lighted taper near them. As soon as they inflame, begin to collect the gas; and when you have filled three bottles, withdraw the delivery tube from the water.

Experiment I.—Set an inverted bottle of the gas on the ring of a retort-stand, and apply a light; the gas burns with a bluish non-luminous flame.

Experiment II.—Pour a little lime-water into the bottle used in the last experiment, when the flame has gone out; on shaking the bottle you learn, from the turbidity in the lime-water, that carbon dioxide is present. One of the products of the oxidation or burning of marsh gas is therefore carbon dioxide.

Marsh gas is formed in coal mines, where it is known under the name of ‘fire-damp.’ If mixed with ten volumes of atmospheric air it forms an explosive mixture, producing water and carbon dioxide. This latter gas will not support life; hence the dreadful effects produced, not only by the actual explosion in mines, but also by the formation of this ‘choke’ or ‘after’ damp, as the carbon dioxide is called by the miners.

Experiment III.—To illustrate the explosive nature of a mixture of marsh gas and oxygen, decant into a soda-water

bottle one volume of the gas, and add two volumes of oxygen ; cork the bottle, shake it, and wrap a cloth tightly round it, then take out the cork, and bring a lighted taper to its mouth ; a very sharp explosion ensues.

Experiment IV.—Fill a perfectly dry flask, capable of holding about 250 c.c., with marsh gas, by upward displacement, and fill also a similar flask with chlorine ; connect these flasks by a glass tube passing through corks in each, and set them in the sunlight, the flask containing marsh gas being uppermost (see fig. 28). You soon notice that the upper as well as the lower flask becomes filled with yellow fumes, but that these after a little time entirely disappear. Now separate the flasks, and bring a bottle containing strong ammonia solution near the mouth of each ; dense white fumes are formed : this, you remember, (Lesson IX.), tells you that hydrochloric acid is present. The chlorine has therefore withdrawn part of the hydrogen from the marsh gas. Another quantity of chlorine combines with the remainder of the marsh gas, forming a new gaseous compound, the presence of which you may detect by its peculiar ethereal odour after agitating the gaseous mixture in the flask with a little water to absorb the hydrochloric acid.

FIG. 28.



You learn then from these experiments—

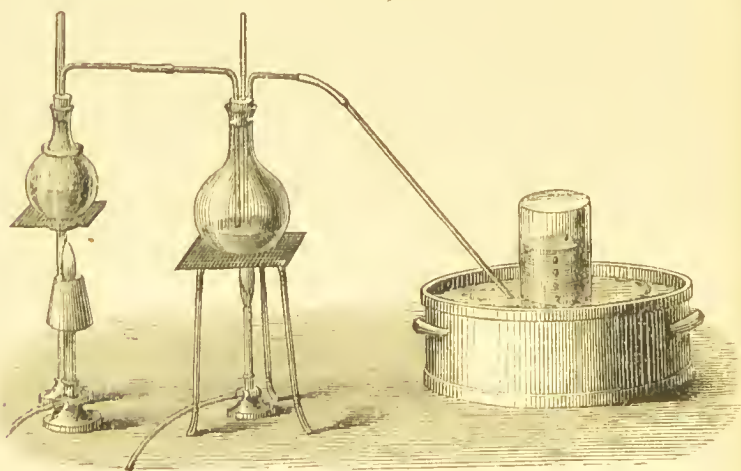
- (1) By what method marsh gas may be prepared.
- (2) That this gas is combustible.
- (3) And that by its combustion carbon dioxide is produced.
- (4) What is the cause of the evil effects produced by this marsh gas when present in mines.
- (5) That chlorine acts on marsh gas in sunlight.

LESSON XVIII.

PREPARATION AND PROPERTIES OF ETHYLENE
(OLEFIANT GAS).

FIT up an apparatus like that shown in fig. 29, consisting of two flasks, the first of which is fitted with a cork carrying a tube bent twice at right angles ; the last limb of this tube dips, through a wider tube, into the second flask, from which a delivery tube leads to the trough. The second flask

FIG. 29.



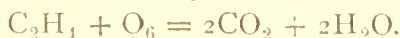
also carries a thermometer, as shown in the figure. Into the first flask pour about 20 c.c. of alcohol (rectified spirits). Mix 40 c.c. of conc. sulphuric acid with 12 c.c. of water, and pour this mixture into the second flask, and fit the corks into their places. Heat both flasks; the alcoholic vapours pass into the sulphuric acid (the temperature of which must not be raised above 170°), the acid gradually darkens in colour, and bubbles of gas come up through the water in the trough. When, on bringing a light close to it, the issuing gas takes fire, you may begin to collect it. Fill

three bottles with ethylene gas, withdraw the lamps, and at once take the delivery tube of the first flask out of the liquid in the second by drawing it up the wider tube. In this reaction the sulphuric acid acts in a manner similar to that noticed in the case of oxalic acid, viz. it withdraws the elements of water :



Experiment I.—Apply a light to the mouth of the first bottle standing on the table ; the gas burns with a bright white smoky flame, while the taper is extinguished. Ethylene is therefore a combustible gas. After the combustion is over, add a little lime-water to the bottle, and shake it briskly ; the turbidity of the liquid indicates the presence of carbon dioxide.

Experiment II.—Graduate a soda-water bottle into four divisions (see Lesson III.), and decant into it one measure of ethylene gas, and three measures of oxygen ; cork the bottle, surround it with a cloth, and shake it several times ; on withdrawing the cork and applying a light, a loud explosion occurs. You have in this experiment completely oxidised the carbon and hydrogen of the ethylene, carbon dioxide and water being the products :



Experiment III.—Pour a few drops of bromine into a small flask, shake the flask, and pour the excess of bromine back into the bottle ; bring the flask, mouth downwards, into one of the bottles of ethylene. The red vapours quickly disappear, while heavy oily drops form on the sides of the bottle, and run down to the bottom. This oil is a compound of ethylene with bromine. A similar oily compound is produced by the union of this gas with chlorine ; hence the name *olefiant* or *oil-producing* gas sometimes given to ethylene.

* This reaction probably occurs in two stages ; in the first ethyl sulphuric acid is formed, and this is then split up into ethylene and sulphuric acid. A mixture of 50 c.c. of methylated alcohol and twice the volume of conc. sulphuric acid, with a quantity of sand to diminish frothing, may be used.

Experiment IV.—Graduate a gas bottle into three equal parts, fill it with water at the trough, and quickly decant up into it two measures of chlorine and one of ethylene ; cover the mouth of the bottle with a glass plate, remove it from the trough, agitate it briskly, and apply a light ; the gases burn with a very smoky flame, which gradually passes down the bottle, much carbon being deposited. This experiment further illustrates the great affinity which chlorine has for hydrogen ; the ethylene is robbed of its hydrogen and the carbon is deposited on the glass.

In this lesson you have learned—

- (1) What is the action of conc. sulphuric acid upon alcohol.
- (2) By what mode ethylene is prepared.
- (3) That ethylene is a combustible gas, burning with a smoky flame. (Coal gas owes its luminosity in great measure to the presence in it of ethylene.)
- (4) That for its complete oxidation or burning, one volume of ethylene requires three volumes of oxygen.
- (5) That with chlorine and bromine ethylene forms oily compounds.
- (6) But that with different proportions of this gas and chlorine the hydrogen of the former is seized upon by the latter, carbon being liberated. Compare this with the action of chlorine upon methane (last Lesson), whereby a *substitution* product of the methane (that is, a product in which part of the hydrogen is replaced by another element) and hydrochloric acid are produced.

- (7) That the explosion which occurs when a light is brought into a mixture of coal gas and air is caused by the combination of the methane, ethylene, and free hydrogen, contained in the gas, with the oxygen of the air.

LESSON XIX.

PREPARATION AND PROPERTIES OF ACETYLENE.

THIS gas is produced in many cases of incomplete combustion of organic substances ; thus, when a Bunsen lamp burns down, the gas is only partially consumed, acetylene is produced, and can be recognised by its peculiar smell. This gas combines with certain metals, as copper, &c. The compound produced when acetylene is passed through an ammoniacal solution of cuprous chloride is very characteristic, possessing a bright red colour ; we make use of this reaction in order to detect the presence of acetylene.

Experiment I.—Make a solution of cuprous chloride by dissolving 10 grams of black cupric oxide in about 100 c.c. of ordinary hydrochloric acid, boil for 15 minutes with 8 grams of metallic copper in small pieces, pour this solution into about one litre of water, allow the precipitate to subside, pour off the water, and rinse the precipitate into a bottle,—of about 150 c.c. capacity,—nearly full of water. After the subsidence of the precipitate, the water is again poured off, 40 grams of powdered ammonium chloride are added, the bottle is again filled with water and shaken up.

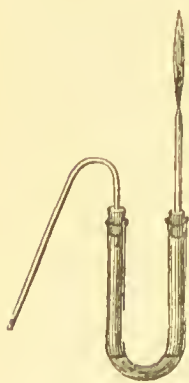
To a small quantity of this solution gradually add ammonia until the precipitate which forms redissolves, and you have an azure-blue solution. Pour a few cubic centimetres of this solution into a wide-necked flask, capable of holding about half a litre, rinse the flask with the liquid and allow it

to drain for a few moments ; turn down a Bunsen burner so that it may *burn below*, and now bring the flask, mouth downwards, a little way over the top of the lamp, and support it in this position on a retort-stand ; after a few minutes you will notice that the inside of the flask becomes coated with a red substance, which is the compound produced by the action of acetylene upon cuprous chloride solution. It is termed copper-acetylene ; the composition is $C_2Cu_2.H_2O$, or perhaps $C_2H_2Cu_2O$.

To show the presence of acetylene in coal gas, we will perform—

Experiment II.—Choose a U-tube each limb of which is about 12 or 15 cm. long and 1 cm. diameter, and fit into each of the openings a cork carrying a little piece of glass tubing ; let one of these tubes be drawn to

FIG. 30.



a tolerably fine opening, to the other attach a caoutchouc tube connected with the gas tap ; pour into the U-tube sufficient ammoniacal cuprous chloride solution to fill the bend, support the tube on a clamp or retort-stand and turn on the gas, which, bubbling through the solution in the bend of the tube, issues from the small glass tube, where it may be lighted (fig. 30) ; after some time you notice the formation of a copious red precipitate in the blue solution, which proves the presence of acetylene in the coal gas.

You have learned—

- (1) That acetylene is produced in very many cases of incomplete combustion.
 - (2) That acetylene is present in coal gas.
 - (3) How to detect acetylene.
-

LESSON XX.

STRUCTURE OF FLAME.

FROM the experiments performed in Lesson III. you have learned the exact relation which exists between the terms 'combustible' and 'supporter of combustion,' and from various experiments you have learned what is meant by the term 'combustion.'

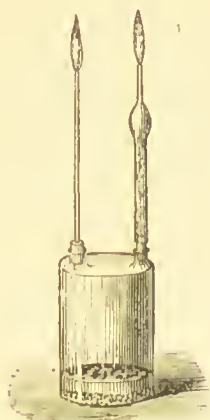
In Lesson XVIII., Experiment I., you saw that ethylene burns with a smoky, *luminous* flame.

Experiment I.—Set up the apparatus used in preparing ethylene (fig. 29, p. 68), putting about 10 c.c. of alcohol and a corresponding amount of sulphuric acid into the flasks; to the end of the delivery tube adapt, by means of caoutchouc tubing, a small glass tube having a tolerably fine orifice. Fill a large wide-mouthed bottle with oxygen; when ethylene gas is coming off in a gentle stream, light it; it burns with a smoky flame. Now bring the bottle of oxygen gas, mouth downwards, over the burning gas; the flame becomes much less luminous and more elongated. You thus see that when this gas is completely burned, or oxidised, the luminosity of the flame is diminished.

Experiment II.—Fit a two-necked bottle with corks, through one of which passes a small glass tube drawn to a tolerably fine point, and through the other a chloride of calcium tube, in the bulb of which is a little cotton-wool which has been previously soaked in benzene. In the bottle place materials for generating hydrogen (see fig. 31). When the gas has been coming off for a little time, test it by filling a test-tube by upward displacement and bringing this near a flame; if the hydrogen burns quietly in the tube, you know that the air has been driven entirely out of the bottle. Now light the gas issuing from both necks of the bottle. The flame of the hydrogen burning at the mouth of the small glass tube is almost colourless, while that at the

mouth of the other tube is highly luminous. The gas giving the latter flame passes, before being burned, through wool

FIG. 31.



soaked in benzene, which is a hydrocarbon, or compound of carbon and hydrogen, resembling in this respect ethylene. When these hydrocarbons burn, carbon is separated and so gives luminosity to the flame.

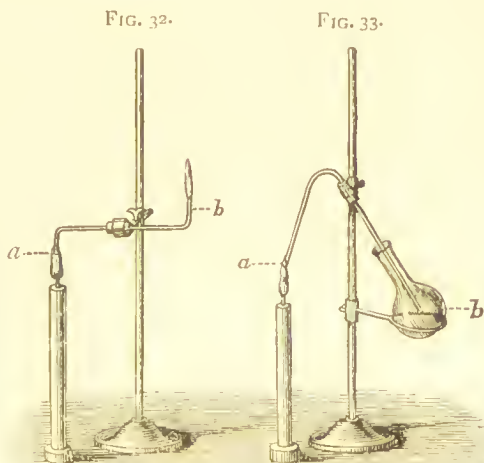
Experiment III.—Fill two bottles with chlorine by downward displacement, and bring one of these over a Bunsen lamp which is burning with a small flame; the luminosity of the flame is much increased.

You have learned that chlorine reacts with ethylene, methane, &c. (components of coal gas), and also that chlorine has a great affinity for hydrogen. Both of these actions probably occur in the present case, and hence, on account of the density of the products of combustion, but more especially on account of the presence of solid carbon, the luminosity of the flame is much increased.

Experiment IV.—Set up a small hydrogen-generating apparatus containing zinc and dilute sulphuric acid and having a platinum jet adapted to the end of the delivery tube. After sufficient time has elapsed to allow of the expulsion of the air from the apparatus, light the issuing gas. The little platinum jet may be extemporised by rolling a piece of platinum foil round a stout piece of wire, say of the thickness of a knitting needle, withdrawing the wire and inserting the roll into the end of the glass tube which if necessary may be narrowed slightly, like the jet of a wash-bottle. On bringing the burning hydrogen into the second bottle of chlorine an increase in the luminosity of the flame is noticed. The product of combustion of hydrogen in chlorine—hydrochloric acid—possesses a density twice as great as that of the

product of combustion of hydrogen in air, viz. water ; therefore the flame appears brighter when the bottle of chlorine is brought over the burning hydrogen. In this case the presence of solid matter in the flame is impossible.

Experiment V.—Bend a glass tube, about 60 cm. long, into the shape shown in fig. 32 ; bring the end *a* into the flame of a candle immediately above the wick ; on applying a light to *b*, you find that combustible gases are being withdrawn from the flame.



Experiment VI.—Move the end *a* of the tube until it is situated at the outside of the candle flame ; a light now brought to the end *b* is extinguished, telling you that a non-combustible gas is present. Allow the end *b* of the tube (fig. 33) to dip into a small flask, into which, after a little time, pour a few cubic centimetres of lime-water ; on shaking the bottle a precipitate forms in the solution. The gas which you have drawn off is therefore carbon dioxide. These experiments tell you that in the flame of a combustible carbonaceous substance there is an inner zone in which the gases are but partially burned, then a zone containing carbonaceous matter

(constituting the luminous part of the flame), while outside of this is the zone of complete combustion in which all the carbon is burned to carbon dioxide. The presence, in this part of the flame, of the product of combustion of the hydrogen, viz. water, may be shown by bringing a test-tube, containing a little cold water, into the outer flame of the candle; drops of dew are immediately formed on the tube, by the condensation of the water vapour on the cold glass.

There is yet another part of the flame, called the *mantle*, which is situated at the extreme outer edge of the flame.

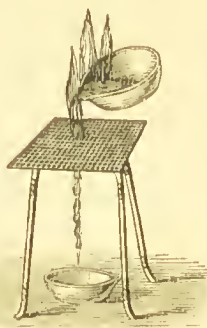
FIG. 34.



FIG. 35.



FIG. 36.



and only becomes visible by holding a piece of cardboard (cut so as exactly to cover all that part of the flame ordinarily visible) between the eye and the flame (fig. 34); the mantle will then be seen round the outer edge of the cardboard.

Experiment VII.—Make a small helix of copper wire (see fig. 35), leaving a space between each coil, and bring this over the flame of a candle; the flame is extinguished. Heat the helix to redness and again bring it over the flame: the flame is not extinguished. The helix did not therefore extinguish the flame by cutting off the supply of air, but by lowering its temperature.

Experiment VIII.—Pour a quantity of burning alcohol

on to a piece of wire gauze held over a basin (fig. 36). The spirit passes through the gauze, but it is no longer ignited. The gauze presents to the burning spirit a large metallic surface, which conducts away heat from the flame, so that the process of rapid oxidation of the constituents of the spirit ceases, and the flame therefore goes out. The same thing occurred in Experiment VII. The copper wire so quickly conducted away heat from the candle flame, that the temperature required to inflame the mixture of gases could no longer be maintained. On this principle of extinguishing a flame Sir Humphry Davy based his celebrated 'safety lamp.'

In this lesson you have learned—

- (1) Something about the difference between a luminous and a non-luminous flame.
- (2) Something about the constitution of a candle flame, as the type of other flames.
- (3) That a flame may be extinguished by heat being conducted from it by a metallic surface.

LESSON XXI.

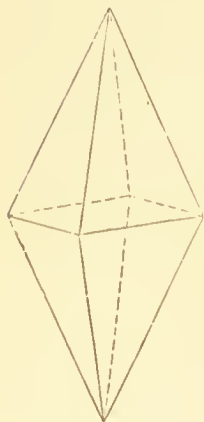
PROPERTIES OF SULPHUR.

Experiment I.—Heat a quantity of 'flowers of sulphur' in a Florence flask placed on wire gauze on a retort-stand. You notice that the sulphur melts, forming a clear mobile liquid, it then darkens and gets thicker, and, as the heat is increased, it again becomes fluid. When this point is reached, take hold of the flask with a cloth or pair of crucible tongs, invert it, and pour the molten sulphur into cold water in a beaker. The mass of sulphur in the water retains its plasticity, and can be moulded with the hand, like recently melted caoutchouc.

When sulphur is allowed to spontaneously crystallise

from its solution in carbon disulphide, it forms *octahedral* crystals of forms derived from that shown in fig. 37; but, as you will learn from the next experiment, it may also be obtained in another crystalline form.

FIG. 37.



Experiment II.—Melt 20 grams of sulphur in a Hessian crucible placed in a fire, and allow it to cool until a crust forms on the surface of the mass; now make two holes in this crust with a glass rod, and invert the crucible so that the still molten sulphur flows out at one of the holes into a dish of water, while air enters at the other. On removing a portion of the sulphur with a knife, you will find that the inside of the crucible is

full of *needle-shaped* or *prismatic* crystals of sulphur.

You have already learned that sulphur burns in air or oxygen, producing the gas sulphur dioxide.

Experiment III.—Fuse a small quantity of sulphur, mixed with an equal quantity of sodium carbonate, in a porcelain crucible over a Bunsen flame, when cool pour a little water into the crucible and dip a silver coin into the solution. The silver is stained black owing to the production of silver sulphide. This reaction is occasionally used for the detection of sulphur.

From these experiments you learn—

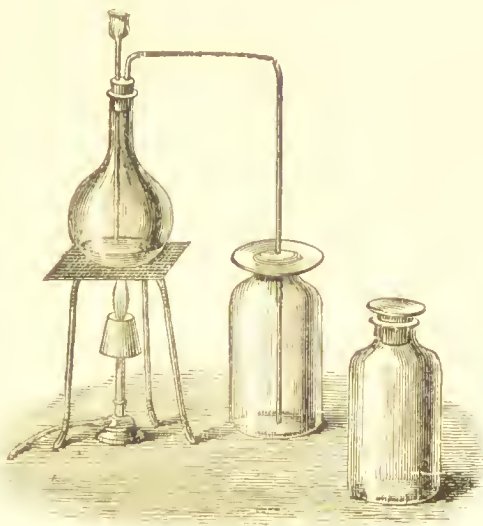
- (1) What is the action of heat upon sulphur.
- (2) By what method the presence of sulphur may be detected.
- (3) That sulphur is capable of existing in various forms, viz. as plastic, octahedral, or prismatic sulphur. Such varieties of one and the same substance are called *allotropic* modifications of that substance.

LESSON XXII.

PREPARATION AND PROPERTIES OF SULPHUR DIOXIDE AND TRIOXIDE.

INTO the flask of an apparatus similar to that represented in fig. 38, put about 20 grams of copper clippings (take care to slide the pieces of copper down the side of the flask to prevent cracking it), and add, through the funnel tube, 60 c.c. of conc. sulphuric acid. Set the flask on a retort-stand,

FIG. 38.



and let the delivery tube dip into a gas bottle. Place a Bunsen lamp beneath the flask and gradually increase the temperature; after a little while you will notice a brisk action going on in the flask; when the action has thus begun, you may lower the lamp flame. You soon perceive that the gas which is given off has a very pungent sulphurous odour. It is identical with the gas produced by burning sulphur in oxygen, viz. sulphur

dioxide : $2\text{H}_2\text{SO}_4 + \text{Cu} = \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$. Collect two bottles of the gas, and while the evolution of the gas is proceeding, get ready an apparatus in which to *liquefy* the sulphur dioxide. Choose a piece of stout glass tubing about 2 cm. diameter ; at a distance of 20 cm. from one end soften the tube in the flame (in the case of thick tubing such as this, it is better to use the blowpipe, *very gradually* increasing the heat of the flame), and draw it out; by heating the projecting portion in the flame, touching it with a little piece of glass-rod, and sharply drawing it off, you will get rid of most of this part ; finally, heat the end of the tube to redness, keep turning it round, and blow in at the open end once or twice; you will thus get a tube sealed neatly at one end.

Now heat the tube at about 8 cm. or so from the open end, and gently draw it out until the narrow part is just a little wider than the delivery tube of the gas-generating apparatus (fig. 39). Select a beaker whose height is about equal to the length of the tube you have just prepared; set this, with its open end upwards, in the middle of the beaker, and surround it with a freezing mixture made by intimately mixing together one part of pounded ice with about one and a half parts of salt.



By this time the two gas bottles will be full of sulphur dioxide, cover them with greased glass plates, and bring the delivery tube into the wide tube standing in the freezing mixture, so that it may reach nearly to the bottom of this tube. Allow the evolution of gas to proceed for some time ; meanwhile examine that which you have collected.

Experiment I.—Plunge a lighted taper into one of the bottles ; the flame is extinguished, and the gas does not take fire ; quickly replace the glass plate.

Experiment II.—Plunge a few flowers (preferably red roses or reddish-coloured pansies) into the same bottle of sulphur dioxide. The red colour of the flowers is after a little time discharged. The gas, therefore, possesses

the property of bleaching ; further experiments will explain this more fully.

Experiment III.—Invert the second bottle beneath water in the trough, and withdraw the glass plate ; the water rises in the jar, showing that the gas is soluble in water. Slip the hand beneath the mouth of the bottle, remove it from the water, and shake it briskly ; again bring it under the water and repeat the operation until the water has nearly filled the bottle. This solution contains *sulphurous acid*— $\text{SO}_2 + \text{H}_2\text{O} + \text{Aq} = \text{H}_2\text{SO}_3\text{Aq}$.

Experiment IV.—Transfer a few cubic centimetres of this solution to a test-tube, and add a drop or two of barium chloride solution ; a white precipitate is produced ; add a few drops of hydrochloric acid, the precipitate dissolves. Boil a second portion of the sulphurous acid solution with a few drops of nitric acid, and again add barium chloride ; the immediate formation of a white precipitate, which is insoluble in hydrochloric acid, shows that there is a difference between this and the original liquid. This white precipitate with barium chloride, as you will afterwards more fully learn, tells us that *sulphuric acid* is present. The sulphurous acid has, therefore, been changed to sulphuric acid, i.e. it has taken up oxygen, $\text{H}_2\text{SO}_3 + \text{O} = \text{H}_2\text{SO}_4$. It is in this way, viz. by robbing substances of their oxygen, or acting as a *reducing agent*, that sulphur dioxide bleaches.

Experiment V.—To a few cubic centimetres of sulphurous acid solution add a little bromine water and boil the mixture. On applying the test for sulphuric acid—viz. barium chloride—to a portion of the liquid, the formation of a white precipitate, insoluble in hydrochloric acid, tells us that this acid has been formed.

The action which has here taken place is analogous to that noticed in the last experiment. The oxygen of the water has been seized upon by the sulphur dioxide, while the hydrogen which remains has combined with the bromine to form hydrobromic acid. To prove the presence of the latter

substance, add a little silver nitrate solution to another part of the liquid; a nearly white precipitate of silver bromide is immediately produced.

Experiment VI.—Pour a small quantity of a solution of potassium iodide into a beaker, add some water and a few drops of starch paste, then one or two drops of chlorine water; as you have already learned, an intense blue-coloured solution is thus obtained. To this solution add, drop by drop, with constant stirring, sulphurous acid solution until the blue colour is entirely discharged. This bleaching is effected by the sulphurous acid combining with the oxygen of the water to form sulphuric acid, while the hydrogen of the water combines with the iodine liberated from the potassium iodide to form hydriodic acid, which, as you know, is colourless, soluble in water, and without action on starch.

You thus learn that sulphur dioxide bleaches in a way directly opposed to that in which chlorine bleaches; the former acts by *reduction*, i.e. by taking away oxygen: the latter by *oxidation*, i.e. by giving oxygen.

You must now turn your attention to what is going forward in the tube in the freezing mixture. If a steady flow of gas has been kept up, you will find, on raising the tube partially out of the beaker, that it contains a liquid; by the application of cold you have caused the gaseous sulphur dioxide to become liquid. Keeping the tube as much as possible in the freezing mixture, direct a blowpipe flame on to the narrowed portion; when fused draw this out, but do not quite close it; allow the tube to get quite cold, again heat the narrow part, and now quickly draw it off. You may remove the tube from the beaker and set it aside; the sulphur dioxide will remain liquid in the closed tube.

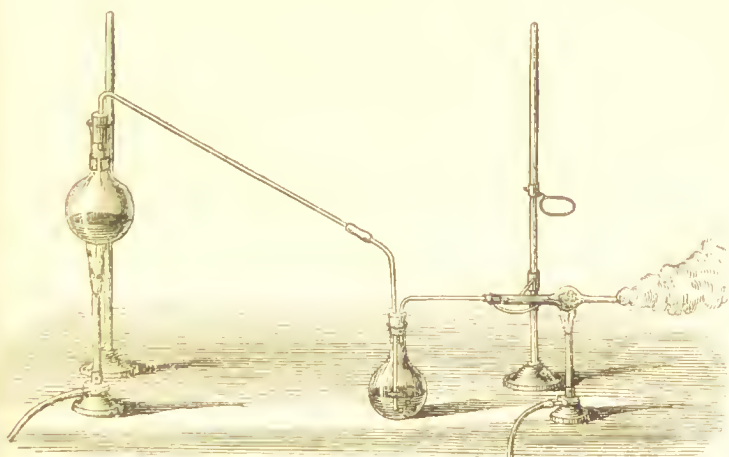
Experiment VII.—Heat a few drops of the sulphurous acid solution in a test-tube. You distinctly smell that sulphur dioxide is given off. Let us try to oxidise this sulphur

dioxide, and thus produce the higher compound of sulphur with oxygen, viz., sulphur trioxide.

Experiment VIII.—Pass a stream of sulphur dioxide into a part of the solution of sulphurous acid, until the liquid smells strongly of the gas; then transfer it to a small flask, fitted with a cork, in which two holes are bored; through one of these passes a tube, which reaches nearly to the bottom of the flask, while through the other a shorter tube is fitted which ends just below the cork.

Fit up a small oxygen-generating apparatus, but let the

FIG. 40.



end of the delivery tube be bent at an obtuse angle with the longer part of the tube. Support the flask on a stand, and connect the delivery tube with the tube coming from the small flask. Take a few pieces of asbestos, soak them in platinum tetrachloride solution, then dry and strongly heat them in a small basin over a Bunsen lamp. The platinum tetrachloride is decomposed, chlorine being given off, while platinum remains behind in a finely divided state, covering the asbestos, which therefore appears nearly black. Put this platinised asbestos into the bulb of a chloride of calcium

tube, and through a cork in the wider end of this tube pass the short tube leading from the flask. The apparatus is represented in fig. 40.

Cause a gentle stream of oxygen to pass through the solution of sulphurous acid in the flask ; the oxygen carries along with it some of the sulphur dioxide, the presence of which is easily distinguished by the smell of the gases issuing from the bulb tube. On gently heating the bulb containing the platinised asbestos, the two gases, oxygen and sulphur dioxide, are caused to unite. Sulphur trioxide, SO_3 , is hereby produced, the presence of this compound being shown by the dense white fumes which now appear near the orifice of the bulb tube. This property of fuming in the air is characteristic of the trioxide.

By means of caoutchouc tubing, adapt to the end of the bulb tube a small glass tube, bent at right angles, and allow this to dip into a little water in a beaker. Continue to heat the bulb, and dissolve the resulting sulphur trioxide in the water. After a little time test some of this water with barium chloride ; you find that it contains sulphuric acid. You have therefore produced this acid by the combination of sulphur trioxide with water :



Experiment IX.—Pour about 10 c.c. conc. Nordhausen sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) into a little retort, to which a small receiver is attached. On heating the acid in the retort, fumes of sulphur trioxide are formed, which pass over into the receiver, where they condense to a white crystalline solid :



If the receiver be carefully closed, these crystals of sulphur trioxide may be kept for a long time. Allow a drop of water to fall on to one of the crystals : the chemical combination is so intense, that the water hisses as if it had touched red-

hot iron. You already know that sulphuric acid is the product of this reaction.

From the experiments in this lesson you learn—

- (1) What are the methods for preparing the two oxygen compounds of sulphur, viz., the di- and tri-oxide.
 - (2) What is the way in which sulphur dioxide bleaches.
 - (3) What is the action of this gas on a solution of iodide of starch. This action, as you will hereafter learn, constitutes the basis of a widely applicable quantitative process.
 - (4) That sulphur dioxide may be liquefied.
 - (5) That sulphur trioxide is the product of the oxidation of sulphur dioxide, and that this compound, in contact with water, yields sulphuric acid.
-

LESSON XXIII.

PROPERTIES OF SULPHURIC ACID.

To make sulphuric acid by the process adopted on the manufacturing scale requires a more complicated arrangement of apparatus than is readily put together in the laboratory. We shall, therefore, neglect the actual preparation of this substance, and proceed to perform a few experiments with the acid, which is a liquid in constant use in the laboratory.

Experiment I.—To a drop or two of sulphuric acid diluted with water, in a test-tube, add barium chloride solution; a copious white non-crystalline precipitate is at once produced. After boiling, allow the precipitate to

settle, pour off the clear liquid, add water to the precipitate, shake it up, and again allow it to settle. After thus washing it several times *by decantation*, pour over the precipitate a little dilute hydrochloric acid; the precipitate remains undissolved. Pour away the hydrochloric acid, and add a little nitric acid; the precipitate is unacted upon. The formation of a white precipitate (barium sulphate), *insoluble in hydrochloric and nitric acids*, when barium chloride is added to any given solution, tells us that sulphuric acid or a sulphate is present in that solution.

Experiment II.—Heat a little of the acid, and pour it on to a small piece of sugar in a porcelain basin. The sugar is instantly charred; steam is given off, while black masses of charcoal remain. Sulphuric acid chars sugar, which has the composition $C_{12}H_{22}O_{11}$, by removing the elements of water, viz., hydrogen and oxygen, and eliminating the carbon.

You thus learn—

- (1) In what way sulphuric acid may be recognised.
- (2) That this acid has a great avidity for water.

LESSON XXIV.

PREPARATION AND PROPERTIES OF SULPHURETTED HYDROGEN.

Fit up an apparatus like that in fig. 41, and in the flask A place some ferrous sulphide. Cover it with water, and pour a little commercial hydrochloric acid through the funnel tube into the flask. After a time sulphuretted hydrogen gas is evolved, and is washed by passing through water contained in the small flask B. The reaction is as follows: $FeS + 2HCl_{Aq} = FeCl_{2Aq} + H_2S$. Allow the exit tube to dip into a dry glass bottle; place the whole apparatus in the draught chamber, and continue the evo-

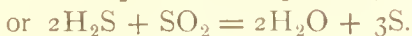
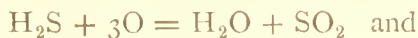
lution of the gas for some time. Now close the bottle with a well-greased plate, remove it, and place in its stead a beaker containing water.

Fig. 41.



Experiment I.—Withdraw the glass plate, and bring a lighted taper to the mouth of the bottle containing the gas. The gas burns with a pale bluish flame, and a slight deposit of sulphur is seen on the bottle. In this reaction sulphur dioxide and water

are produced together with the sulphur, some at least of the sulphur being produced by the interaction of the sulphur dioxide and the unburnt sulphuretted hydrogen.



If the gas be mixed with air in quantity sufficient to burn it completely, the first reaction alone takes place.

The water in the beaker glass will now be saturated with sulphuretted hydrogen, and will smell of that gas.

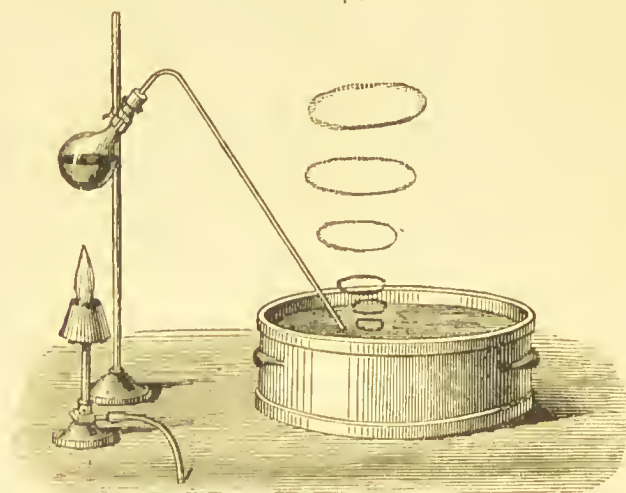
Experiment II.—Prepare solutions of copper sulphate, arsenious oxide, ferric chloride, and barium chloride in water, acidulate them slightly with hydrochloric acid, and add to each some of the solution of sulphuretted hydrogen. In the first liquid, a black precipitate of copper sulphide (CuS) will be produced; in the second, a yellow precipitate of arsenious sulphide (As_2S_3); in the third, a finely divided precipitate of sulphur; the fourth liquid will remain clear. By taking advantage of the reaction of metallic solutions towards sulphuretted hydrogen, we are enabled to arrange the metals in groups for the purposes of qualitative analysis. (See p. 107.)

LESSON XXV.

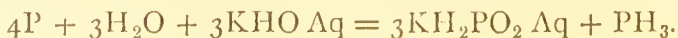
PREPARATION AND PROPERTIES OF PHOSPHORETTED
HYDROGEN.

FIT a cork carrying an exit tube into a small round-bottomed flask supported on a clamp, in which you have placed a fairly conc. solution of caustic potash and a few pieces of phosphorus. Connect the end of the exit

FIG. 42.



tube, by means of a caoutchouc tube, with the gas tap, and pass coal gas into the apparatus, the cork being loosely held in its place, until the air in the apparatus is entirely displaced by the coal gas. Now shut the gas tap, remove the caoutchouc tube, fit the cork tightly into the flask, and quickly plunge the end of the exit tube under water in a pneumatic trough. On now heating the flask a gas is evolved, each bubble of which, as it passes out of the water into the air, spontaneously inflames, and produces a ring of white smoke (see fig. 42). The chief reaction which takes place may be thus formulated :



The rings are composed of phosphoric anhydride, formed by the burning of the phosphoretted hydrogen ($2\text{PH}_3 + 8\text{O} = \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$).

In this lesson you learn by what method phosphoretted hydrogen is prepared, and also that the gas as thus prepared is spontaneously inflammable.

PART II.

QUALITATIVE ANALYSIS.

QUALITATIVE ANALYSIS is that branch of Practical Chemistry which treats of the methods of determining the qualitative composition of compounds and mixtures of compounds. By far the greater number of substances may be resolved into parts or constituents, which separately are possessed of properties different from those that characterised the original matter. These parts may, generally, be again broken up; but ultimately we arrive at certain kinds of matter from which no simpler substances have yet been obtained.

These ultimate kinds of matter we term *Elements*; the substances formed by the union of these in definite proportions we term *Compounds*. For example, a piece of chalk (calcium carbonate) when heated is split up into two groups or combinations of elements—carbon dioxide, which is evolved; and lime, which remains behind. By appropriate means we can further resolve the carbon dioxide into carbon and oxygen, and the lime into calcium and oxygen; but all attempts to break up the calcium, the carbon, or the oxygen into simpler substances have hitherto been unsuccessful: these three substances, calcium, carbon, and oxygen, are therefore called elements.

If, then, we desire to know of what substances a given piece of matter is composed, our wish will be satisfied when

we have ascertained what elements, or what combinations of elements, are present in it.

The total number of the elements at present known to us is about seventy, but comparatively few of these are of common occurrence, and still fewer have received any applications in the arts or manufactures.

The operations of Qualitative Analysis may be conveniently subdivided under the two heads of (1) Analysis by dry reactions ; and (2) Analysis by wet reactions.

In determining the composition of a substance by the dry method, we subject it to examination when in the solid state ; for example, we notice if it imparts any peculiar colour to flame ; if it yields a metal when heated with reducing substances at a high temperature ; or if, when heated, it imparts a colour to various fluxes, &c.

In analysing a substance in the wet way, we subject it to the action of appropriate solvents, and determine the composition of the substances dissolved by the addition of reagents, themselves also in solution.

SECTION I.

GENERAL PRELIMINARY OPERATIONS.

A. *FLAME REACTIONS.*

THE flame of the Bunsen lamp may be used to detect the presence of very many elements.

The Bunsen lamp consists essentially of a metal tube, at the bottom of which a gas burner is fixed ; the lower part of this tube is pierced with holes, through which air enters and mixes with the gas in the tube. These holes are of such a size as to admit an amount of air sufficient to form, with the gas issuing from the burner, a non-luminous but very

hot flame. The volume of the air is usually about $2\frac{1}{2}$ times that of the gas.

The Bunsen lamp to be used in the following experiments is shown in fig. 43, No. 1. At *a* is a circular cap, by moving which you can regulate the supply of air, so as to obtain a more or less luminous flame. A conical chimney, resting on the gallery (*b*) of the lamp, serves to protect the flame from draughts of air.

The flame is shown in fig. 43. No. 2, of its natural size ; the letters refer to the various portions of the flame, with the properties of which it is necessary that you make yourself thoroughly acquainted.

There are three principal divisions, viz.—

- (1) The dark zone, *a a*, in which the cold, unburnt gas is mixed with about 62 per cent. of air.
- (2) The flame mantle, *aca*, in which is a mixture of burning coal gas and air.
- (3) The luminous point *aba*, which is not seen when the full supply of air is allowed to enter the lamp, but which can be produced by turning the cap, so as partially to close the holes at *a*, No. 1.

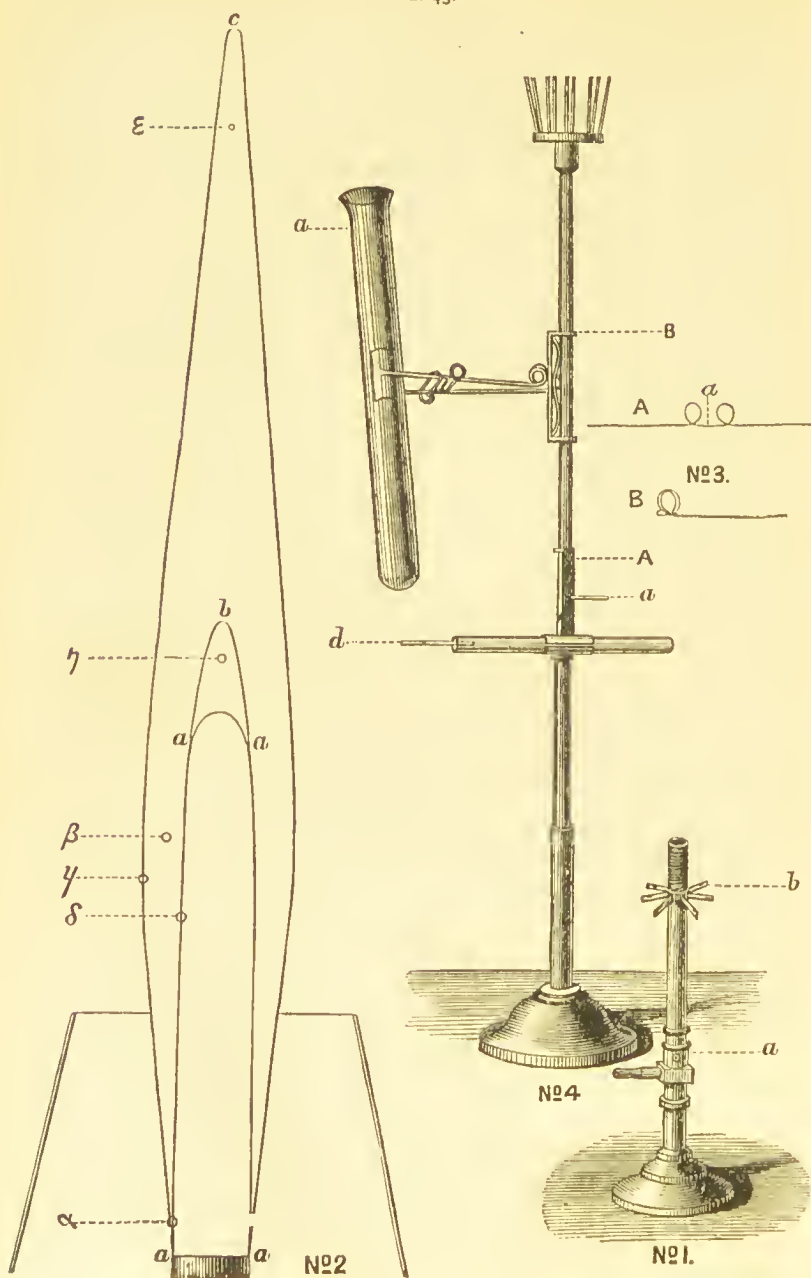
Examining the flame more in detail, we find the following six points, which are made use of in the reactions :—

1. The base of the flame is situated at *a*, a very small distance from the summit of the lamp itself. On account of the proximity of the metal tube, and also by reason of the ascending current of cold air, the temperature of this part of the flame is, comparatively, very low. Many easily volatilised substances may be recognised by the colours which they impart to the flame when held in this portion of it.

2. The zone of fusion, or point of highest temperature, is situated at β , somewhat above the first third of the entire height of the flame, and at a distance from the edge of the flame equal to about one-fourth of its greatest breadth.

3. and 4. The lower, and upper oxidising flames : the former of which, situated at γ in the outer margin of the

FIG. 43.



zone of fusion, possesses a higher temperature than the latter, which is found at ϵ , the highest point of the non-luminous flame when the draught-holes are wide open.

5. and 6. The lower, and upper reduction flames : the former is at δ , close to the dark central zone : owing to the presence of atmospheric oxygen the reducing powers of this flame are not so great as those of the upper reducing flame, which is situated at η , just over the dark zone, and is formed by lessening the supply of air so as to produce a considerable amount of finely divided carbon or of dense hydrocarbons, but not sufficient to form a sooty deposit on a test-tube full of cold water held, for a moment, at this point.

In examining substances by means of these flame reactions, the appliances must all be on the smallest possible scale, otherwise so much heat will be carried off by them as to reduce the temperature of the flame to a point at which the proper reaction can no longer be obtained.

Many substances to be tested are held in the flame by means of a little piece of platinum wire ; this wire must be so thin that one decimeter of it does not weigh more than 34 mgm. If two little loops be made on the wire, as shown in fig. 43, No. 3, A, these may then be so brought together, by turning the wire round at the point a , as to form a little catch in which the substance to be tested rests. (See No. 3, B.) Such a platinum loop is also very useful for holding decrepitating substances, which should first be ground to fine powder with the elastic blade of a small knife (fig. 44, No. 1, p. 97) upon a little porcelain plate, then drawn up on to a square centimetre of moistened filtering paper, which, held in the platinum wire loop, can be burned ; the sample is thus obtained adhering to the wire.

Certain substances cannot be held in the flame on the platinum wire, as they either act upon the metal, or do not adhere to it when moistened ; these are supported on a piece of asbestos about one-fourth the thickness of an ordinary lucifer-match.

In fig. 43, No. 4, is shown an arrangement by means of which substances to be tested may be held in the flame for a length of time. A small glass tube is held by the arm, *a*, attached to the carrier, *A*; into this tube a little piece of platinum wire is fused. The carrier, *A*, is moveable, so that the substance held in the loop of the wire may be moved to any part of the flame, and held there while the phenomena which occur are noted.

The arm, *d*, also attached to the carrier, *A*, serves to support threads of asbestos, which are often used instead of platinum.

Another carrier, *B*, carries an arm which may clasp a small test-tube containing any substance requiring to be held for a length of time in the flame.

From the phenomena noticed when substances are heated we may often learn much concerning them. The following points are more especially to be observed:—

(1) *Emission of Light*.—Heated on the platinum wire in the hottest part of the flame, different substances emit light of different degrees of intensity. If the sample and the platinum wire appear equally luminous, the substance is said to be of mean emissive power; if the wire appears more luminous than the substance, the emissive power of the latter is said to be low, while this same quality is called strong or high if the light emitted by the heated substance be more intense than that coming from the platinum wire.

(2) *The melting point* of many substances may be pretty accurately determined by holding them on the platinum wire, in different parts of the flame, and observing the tints assumed by the wire. The following six different temperatures may thus be obtained: (*a*) below a red heat; (*b*) commencing red heat; (*c*) red heat; (*d*) commencing white heat; (*e*) white heat; (*f*) strong white heat.

(3) *The colour imparted to the flame* by volatilised substances may be judged of by holding the sample in the upper

reducing flame, when the colour appears in the upper oxidising flame.

If we wish to discriminate between substances which impart various colours to flame, we may often do so by bringing the mixture into the lowest and coldest portion of the flame: the most volatile substance is the first to betray its presence, by imparting a momentary colour to the flame; this is followed by the next volatile, and so on.

But perhaps the most important point you have to notice is the behaviour of substances when heated in the oxidising and reducing flames.

I. REDUCTION OF SUBSTANCES.—Very many compounds when exposed to the influence of the reducing flame give up the oxygen, sulphur, etc., which they contain, the metals being thereby obtained in the pure state; to these various tests can then very easily be applied.

Bring a crystal of washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) to the side of the flame, and when the edge begins to melt, smear a common wooden lucifer match, with the head broken off, with the fused salt. By gently heating the smeared match in the flame you obtain a mass of carbonised wood intermixed with sodium carbonate. A small quantity of the substance to be tested is now to be placed on the palm of the hand, and well mixed, by means of the small knife, with a little fused soda crystals. A portion of this mixture you must now cautiously bring on to the end of the prepared match. This is, perhaps, the most difficult part of the process, as in attempting to make the substance adhere to the match, the carbonised mass is very apt to break off. Heat the match with the substance on it in the lower reducing flame, situated at δ ; the soda effervesces; after a few moments withdraw the match, break off the head into a small agate mortar, press it gently with the pestle, adding a little water; the lighter particles of carbon float upon the water, the soda is dissolved, and the heavy reduced metal is left, on pouring off the water,

at the bottom of the mortar. After a few washings the metal is obtained almost perfectly pure. You must now examine the small bead of metal. To do this, remove it to a little piece of glass (a piece of a broken flask is the best), and gently dry it over the flame. The colour and general appearance of the small metallic bead will give you some clue to its nature. Copper may be at once recognised by its red colour; lead, by its bluish-grey colour and its malleability; bismuth and antimony, by their brittleness; iron, by the action of a magnetised steel blade upon it; and so on. If the metal is suspected to be iron, the small knife-blade is drawn once or twice over a magnet, and then brought near to the spicules: if these are attracted by the blade, the metal, you may almost certainly conclude, is iron. Nickel and cobalt are also magnetic, but not to so great a degree as iron.

The metal is further to be tested by being brought into solution and having several *wet tests* applied to it. Let us take an actual example.

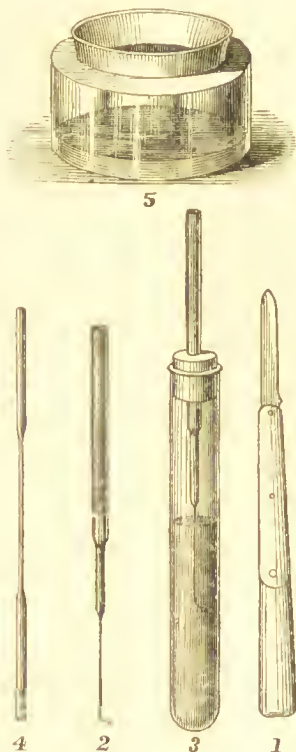
Treat a very small quantity of copper sulphate as directed above. From the red colour of the metal obtained you conclude that it is copper; you must, however, make quite sure of this. For this purpose the reduced metal placed on the small glass plate is dissolved by gently warming it with one drop of dilute nitric acid; the excess of acid is driven off by blowing on the surface of the warm glass; a drop of water is added, and the corner of a small piece of filtering paper being dipped into the solution, a very little of it is sucked up by the paper. On now bringing a drop of potassium ferrocyanide (a reagent used as a test for copper) on to the paper, a brown stain of copper ferrocyanide instantly makes its appearance.

Sometimes it is preferable to use small capillary tubes in the application of the wet tests. To form these, heat a piece of wide thin glass tubing, and when soft draw it out slowly, turning it all the while. The thin part of the tube

(see fig. 44, No. 4) is now separated from the rest, and cut into lengths of about 6 cm. One of these small capillary tubes is dipped into the solution to be tested; a very small quantity of the solution rises a little way in the tube, from which, by gentle blowing into the other end of the tube, it is expelled on to a small piece of glass; a drop of the test reagent is also brought on to the glass in a precisely similar manner, and after slightly stirring the mixture, a drop of it is again brought into a third capillary tube, when any precipitate or change of colour in the liquid is easily detected.

Mix a small quantity of ferrous sulphate with the fused sodium carbonate, bring the mixture upon the charred match, and hold it in the upper reducing area (η) for a minute or so. Break off the charred mass containing the reduced metal into a small mortar in which are a few drops of water, crush it gently with the pestle, and insert the magnetised blade of a knife. The spicules of iron will attach themselves to the blade; they may be washed, without being detached, by allowing a few drops of water to flow along the knife blade, dried, by holding the blade above the flame for an instant, wiped off on to a piece of filter paper, and dissolved in a drop of hydrochloric acid. Dry the paper carefully over the lamp, and moisten the yellow spot with a drop or two of a solution of potassium

FIG. 44.



ferrocyanide : it will be seen to acquire a deep-blue tint owing to the formation of *Prussian blue*.

Treat a little more of the ferrous sulphate on the carbonised splinter with soda in the reducing flame, break off the head of the match on to a silver coin, and moisten it with a drop of water ; in a few moments the coin will be stained brownish-black. This stain tells you that sulphur was present in the substance tested. By the combined action of soda, charcoal, and the reducing flame on the ferrous sulphate, soluble sodium sulphide has been formed, which, acting upon the silver, has given rise to a film of black silver sulphide. Almost all sulphates may be thus reduced, and the sulphur recognised.

You see how very delicate these reactions in the reducing flame are, and how they may be made the means of detecting almost infinitesimal amounts of many substances.

As you learn the various wet tests for the metals, you will be able yourself to apply them to the beads obtained in your preliminary flame reactions.

But let us now glance at another application of this reducing flame : many of the metals may be obtained, by its aid, in the form of *films*.

The following experiments are only applicable to those elements which are volatile at the temperature of the reducing flame.

The principal of these are antimony, arsenic, bismuth, mercury, and cadmium.

Bring a small piece of arsenious oxide on to a thread of asbestos, by slightly wetting the asbestos between the lips and then touching the oxide with it. Into a porcelain basin, about 15 to 20 cm. diameter, glazed on the outside, pour some cold water, and hold the basin close above the asbestos in the upper reducing flame. The arsenious oxide is thus deoxidised, a film of metallic arsenic being deposited on the cold surface of the basin. To this film many tests can now be applied, but these will more properly be performed when

you have gone through the wet tests for arsenic. Meanwhile you must note the appearance of the arsenical film or mirror.

Repeat the above experiment, using an antimony compound (antimony trichloride will do) instead of arsenious oxide, and compare the film thus obtained with that given by the arsenic. You at once notice the sooty-black *velvety* appearance of the antimony mirror. From the appearance of the films you may often be able to tell by what metal they are caused.

Volatilise a small quantity of corrosive sublimate (HgCl_2) in the manner just described. You thus obtain the metallic film of mercury; you see how it spreads over the entire under-surface of the porcelain dish, and how unlike it is in this respect to either antimony or arsenic.

Although we do not as yet proceed to apply any 'wet tests' to these metallic films, you will nevertheless perceive the service which may be rendered to the chemist in his qualitative researches by these easily-obtained mirrors.

II. OXIDATION OF SUBSTANCES.—Repeat the experiments just performed, but hold the asbestos in the upper oxidising flame; you thus obtain films of the *oxides* of the metals upon the porcelain.

Obtain thus an *oxide film* of arsenic, using a small quantity of arsenious oxide. Notice the lavender tint of the flame and remark also the white smoke which rises from it, caused by the volatilised oxide of arsenic. On the porcelain you obtain an almost imperceptible film. This, on the application of proper tests, is very easily recognised to be arsenious oxide. Similar oxide films are obtainable from many other metals.

From these oxide films others are obtained which are very characteristic, and often of great use in helping us to draw conclusions as to what substances we are dealing with.

Iodide Films.—To obtain these, the dish on which we have formed the oxide film is, after being breathed on, placed upon the wide-mouthed well-stoppered glass (fig. 44, No. 5)

which contains fuming hydriodic acid and phosphorous acid, obtained by the gradual deliquescence of phosphorus triiodide.

Iodide films may more easily be obtained by holding a bunch of asbestos, soaked in a solution of iodine in alcohol, underneath the dish on which the oxide film has been produced, and setting fire to the alcohol.

Sulphide Films are easily obtained from the oxide films by blowing the vapour of conc. ammonium sulphide solution over these, and removing excess of the ammonium sulphide by *gently* warming the basin.

FIG. 45.



The ammonium sulphide is contained in a small wash bottle, the exit-tube of which is cut short so as not to dip into the liquid, while the blowing tube passes nearly to the bottom of the flask. (See fig. 45.)

The reduction films should be deposited on a glass tube instead of on porcelain when a considerable quantity of the film is required for examination. In this case a tube similar to that represented in fig. 43, No. 4 *a*, is half filled with water, and it is so arranged as to catch and condense the metallic fumes arising from the substance, which, supported on an asbestos thread by the holder *d* (see fig. 43), is held in the upper reduction flame. This arrangement may be left for some time, until a sufficiently large film has accumulated on the glass. (As the water in the glass soon boils, it is desirable to put a very small piece of marble into it to prevent 'bumping'.)

A few substances when heated with certain solutions in the Bunsen flame yield coloured beads. These beads are generally obtained by bringing a small quantity of the substance to be tested on to one of the platinum wires (see fig. 44, No. 2), heating it for a few moments in the hottest part of the flame, allowing it to cool, and by means of a capillary tube moistening the mass with the solution used as a test, and

again heating in the oxidising Bunsen flame. Heat a very small quantity of zinc sulphate on the loop of the platinum wire, moisten the bead when cold with cobaltous nitrate solution, and heat again in the upper oxidising flame; a beautiful green-coloured mass is proof of the presence of zinc. The special application of these flame reactions to the various metals will be described when we speak of these in detail.

When we have a mixture of substances each of which colours the Bunsen flame, it is often possible to discriminate between them by viewing the flame in which the mixture is held through coloured glasses, or through a glass prism containing indigo solution. The colours imparted to the flame by different bodies are distinguished as : (1) *border colours*, produced by the most volatile substances when held in the loop of a platinum wire a very little way outside of the flame, about 2 mm. from the lower part; (2) *mantle colours*, produced by holding certain substances in the outer part or mantle of the flame; (3) *flame colours*—these colours are shown when the less volatile substances are held in the hottest part of the flame.

A glass prism (fig. 46), filled with dilute indigo solution, is very useful in observing certain flames. The base of the prism may conveniently measure about 35 mm. and its length 150 mm. The indigo solution is made by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, diluting with 1,500 to 2,000 parts of water, and filtering. The flame is first viewed through the thinner layers of the liquid, and gradually through thicker and thicker layers, by moving the prism horizontally.

If small quantities of a sodium salt be mixed with a salt of potassium, the violet colour given to the flame by the latter is completely hidden by the intense yellow of the

FIG. 46.



sodium flame ; no sodium rays can pass through the indigo solution, which, however, freely transmits the potassium rays ; if therefore the mixed flame be viewed through the indigo prism, it appears at first of a sky-blue colour, changing, as it is viewed through thicker layers of the solution, to violet, and lastly appearing crimson-red.

Other applications of these flame tests with coloured glasses will be noticed under the special tests for the various metals.

B. *USE OF THE SPECTROSCOPE.*

Of late years the spectroscope has become of general use in qualitative analysis.

The indications afforded by this instrument are of such exceeding delicacy that by its means $\frac{1}{300000}$ part of a milligram of sodium can be detected with accuracy.

The spectroscope is shown in fig. 47. It consists of a flint glass prism, A, having a refracting angle of 60° , resting on a brass plate which again is fixed on an iron or brass support, B. The brass plate carries also the tube C. The tubes D and E are supported by arms, so as to be moveable in a horizontal plane about the axis of the support B.

On the end of the collimator tube, C, nearest the prism, is placed a lens, the other end being closed by a plate in which there is a vertical slit. The end of the tube E nearest the prism is also furnished with a lens ; at the other end is a reduced photographic millimetre scale, which can be seen through the telescope, D.

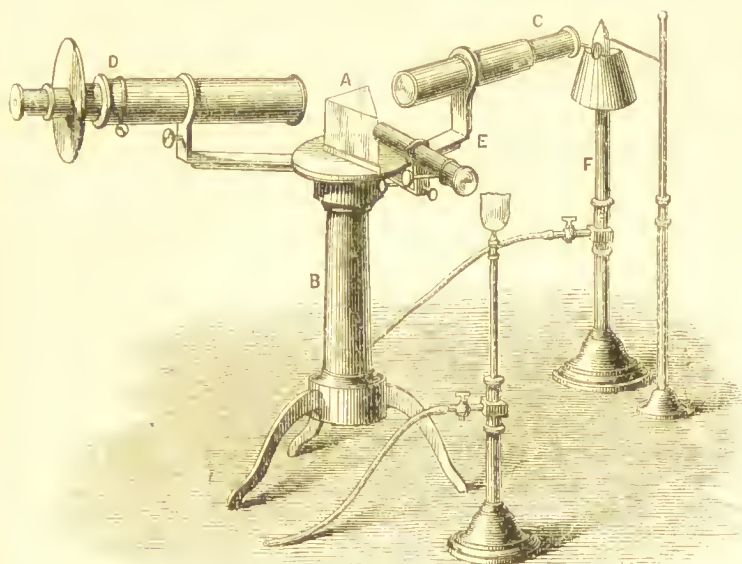
It is sometimes necessary to obtain two spectra in the field of the telescope at the same time, so that we may compare the positions of the lines in each.

The arrangement of the vertical slit in the collimator tube, C, enables us to do this. An enlarged drawing of this arrangement is shown in fig. 48, No. 1. The upper part, *a b*, of the slit is open ; the under part is covered by the small glass prism, *c*. Rays of light falling directly on the upper

part of the slit pass therefore straight into the tube *c*, as shown in fig. 48, No. 2, p. 104, where *A* represents the source of light, and the dotted line *A b* the passage of the rays into the tube.

If at the same time rays proceed from a source of light situated at *B*, they will fall on the surface, *c d*, of the small prism, and will be sent, by total reflection, in the direction *c f b* through the lower part of the slit, also into the colli-

FIG. 47.



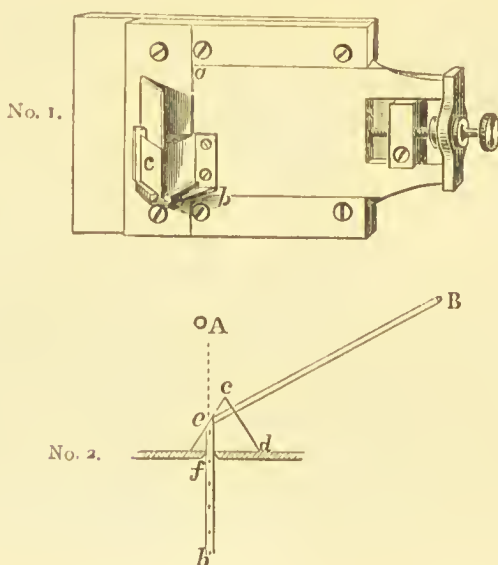
mator tube. By this means we obtain two spectra, one directly over the other, and the coincidence of the lines in each is thus easily observed.

To arrange the instrument, the telescope, *D*, is so adjusted that a distant object is clearly seen by it; it is then fixed in its place, and its axis brought into a straight line with that of *C*, the slit in the latter tube being drawn out, and the telescope adjusted so that the middle of the slit is seen in the middle of the field of view.

The prism is now fixed in its place, and secured by a spring clamp for the purpose. On directing the axis of *c* towards the flame of a candle, and moving the telescope through a certain angle, the spectrum of the flame is seen in the lower part of the field; *E* is now placed so that the image of the scale illuminated by a small gas flame is seen through the telescope *D*.

By means of a small screw on *E* the divisions are

FIG. 48



focussed. The breadth of the slit in *c* can also be regulated by a similar screw. All extraneous rays of light are shut off by throwing a black cloth over the apparatus. The lamp, *F*, is moved until the mantle of the flame is before the slit. Another lamp is also brought into a proper position, if it be desired to examine two spectra simultaneously.

There is another form of spectroscope now come into very general use, in which the small tube carrying the scale is dispensed with. In this instrument the telescope is

moveable upon a graduated circle. The line whose position it is wished to ascertain is brought into the middle of the field of view, and the degrees on the circle are then read off. Several prisms are also often used instead of one; we thus get a higher dispersive power, and consequently a larger spectrum.

In the direct-vision spectroscope (fig. 47 A), which consists of a single tube like a small telescope, the ray of light after entering the slit is refracted and reflected by the prisms in such a manner that it leaves the instrument in the same plane as that in which it entered.

Fig. 47 A.



In using this instrument—which is very compact and serviceable for laboratory use—we look through the tube directly at the object supported in the Bunsen flame. By means of a little device like that described on p. 103, a second spectrum may be sent into the instrument, and the lines of the two spectra compared with one another.

On now bringing a very small quantity of sodium chloride (common salt), supported in the loop of a clean platinum wire, into the mantle of the lamp flame, the yellow line *D_a* is seen strongly marked in the spectrum. This line instantly tells us that sodium is present. Each metal when vapourised, and the vapour heated, exhibits characteristic lines in the spectrum, and by these each is easily recognised. (See Frontispiece.)

It is only when in the state of vapour that the characteristic spectra are afforded by the elements. All solid or liquid substances, when heated, emit light, which, when examined by the spectroscope, is seen at first to consist of red rays only; as the heat increases, other rays are given off, until a point is reached at which, all the luminous rays being emitted, the body is said to be white-hot: such spectra are, therefore, *continuous*, and can afford no indications of the chemical nature of the substance we are examining. The spectra we require are, therefore, dis-

continuous spectra—spectra made up of rays of different and definite degrees of refrangibility. Such spectra we have produced by analysing the light emitted by glowing gases or vapours. Therefore we can only examine, in the arrangement described above, such substances as are volatile at the highest temperature obtainable by the Bunsen lamp. Other substances are frequently volatilised by means of the electric light or by the spark discharge; but for our purposes it will be sufficient only to test by the spectroscope the more easily volatile bodies.

The application of these tests will be given when we come to speak of the metals in detail.

C. *USE OF PRELIMINARY DRY REACTIONS.*

Many substances when heated in a glass tube exhibit phenomena which enable us to decide with tolerable accuracy what elements are present.

Heat a few crystals of sodium sulphate, reduced to powder, in a small glass tube closed at one end. Drops of water speedily appear on the sides of the tube. These tell you that the salt contained water of crystallisation.

In a similar manner heat a few crystals of potassium chlorate. The salt decrepitates, and then partially fuses. A glowing chip of wood on being brought to the mouth of the tube bursts into flame; oxygen is therefore being evolved.



FIG. 49.

Bend a small piece of glass tubing so as to form an obtuse angle (see fig. 49); in the bend place a small quantity of sodium sulphite, and heat this gently. A gas having the smell of burning sulphur is given off.

These experiments may be multiplied greatly; but we mean here merely to point out the great help which preliminary dry reactions yield us in the systematic qualitative examination of an unknown substance. We shall hereafter have opportunities of more fully explaining and developing these reactions.

SECTION II.

SYSTEMATIC QUALITATIVE TESTING.

A. REACTIONS OF THE BASES.

WE shall for the present confine ourselves to the reactions of those metallic bases which are of more common occurrence, viz. :—

Aluminium, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, tin, and zinc.

The above-mentioned metallic bases may be divided into a comparatively small number of groups, in accordance with their deportment towards certain reagents, called *group* reagents.

Each group reagent precipitates, under stated conditions, a certain number of metals, and these metals only; and the addition of one of these reagents, if made in proper order, does not hinder the action of the others; that is to say, if group No. 1 be precipitated, and the precipitate removed by filtration, group No. 2 remains in solution, and is thrown down on the addition to the filtrate of the appropriate group reagent.

In analysing a solution containing bases, it is necessary, in the first place, to divide these bases into groups, and then to examine each group precipitate in detail, and to seek for the special metals present by the application of reagents, which give characteristic reactions with the individual metals.

The group reagents are five in number; their names are given in the order of their application :—

(1) Hydrochloric Acid. (2) Sulphuretted Hydrogen. (3) Ammonia in presence of Ammonium Chloride. (4) Ammonium Sulphide. (5) Ammonium Carbonate.

Group I. comprises all metals whose chlorides are practically insoluble in water, and which are therefore precipitable by hydrochloric acid. These are **silver, lead, and mercury** (monad mercury or mercurous).

Group II. comprises all of the remaining metals whose sulphides are insoluble in dilute acids, and which are, therefore, precipitable by sulphuretted hydrogen from acid solutions. These are **mercury** (dyad mercury or mercuric), **lead, bismuth, copper, cadmium, arsenic, antimony, and tin.**

Group III. comprises all of the remaining metals whose hydrates are insoluble in an ammoniacal solution, and which are, therefore, precipitable by ammonia. These are **iron, aluminium, and chromium** (manganese is partially precipitated with this group).

Group IV. comprises all of the remaining metals whose sulphides are insoluble in an alkaline solution, and which are, therefore, precipitable by ammonium sulphide. These are **nickel, cobalt, zinc, and manganese.**

Group V. comprises all of the remaining metals whose carbonates are insoluble in an alkaline liquid, and which are, therefore, precipitable by ammonium carbonate. These are **barium, strontium, and calcium.**

The remaining bases are not classified in groups.

SPECIAL REACTIONS FOR MEMBERS OF GROUP I.

I. SILVER.—Silver nitrate (AgNO_3) is used for the tests.

1. *Dry Reactions.*—On charcoal splinter (see p. 95), silver gives a white metallic bead, easily soluble in nitric acid; the solution gives a white precipitate with hydrochloric acid.

2. *Wet Reactions.*—Dissolve a few of the crystals in water, and test the solution as follows :—

(a) Hydrochloric acid (HCl) throws down a white curdy precipitate of silver chloride (AgCl); this precipitate is insoluble in hot water, but dissolves in ammonia. On the

addition of nitric acid to the ammoniacal solution, silver chloride is reprecipitated.*

(b) Sulphuretted hydrogen (H_2S) produces a black precipitate of silver sulphide (Ag_2S).

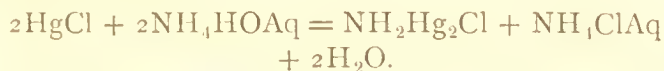
(c) Potassium chromate (K_2CrO_4) throws down dark-red silver chromate (Ag_2CrO_4), soluble in hot nitric acid.

II. MERCURY.—Mercurous nitrate (HgNO_3) is used for the reactions.

1. *Dry Reactions.*—On asbestos thread in reducing flame mercury gives a lustrous metallic film spreading over the basin. By dipping asbestos in a cone. alcoholic solution of iodine, setting fire to the alcohol, and holding the asbestos under the basin, very characteristic carmine-coloured mercuric iodide (HgI_2) is produced.

2. *Wet Reactions.*—Dissolve a few of the crystals in water, and apply the following tests :—

(a) *Hydrochloric Acid.*—A white precipitate of mercurous chloride (HgCl) is thrown down, insoluble in hot water, insoluble in ammonia, but blackened by this reagent, owing to the formation of a di-mercurous ammonium-chloride ($\text{NH}_2\text{Hg}_2\text{Cl}$) :



(b) *Sulphuretted Hydrogen* produces a black precipitate of mercurous sulphide (Hg_2S).

(c) *Stannous Chloride* (SnCl_2) throws down a grey precipitate of metallie mercury.

(d) Put a slip of clean metallie copper into a little of the solution ; a grey stain (metallic mercury) forms on the copper. When rubbed, this stain gets brighter ; it is volatilised by heat.

* In all cases before testing a precipitate as to its solubility in any liquid, it must be collected on a small filter and *thoroughly* washed ; a small portion is then removed to a test-tube and the required reagent added.

III. LEAD.—Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) is used.

1. *Dry Reactions*.—On charcoal splinter, lead salts give soft malleable beads, easily dissolved by nitric acid: the solution gives a white precipitate with sulphuric acid. On asbestos thread in reducing flame, the flame is coloured pale blue, and simultaneously a black or brown metallic film is formed (the colour is dependent on the thickness of the deposit), from which an orange-yellow iodide film, and a brownish-black sulphide film may be obtained.

2. *Wet Reactions*.—Dissolve the remainder of the crystals in water, and test the solution as follows:—

(a) Hydrochloric acid is added; a white precipitate of lead chloride (PbCl_2) forms,* soluble in boiling water (from which solution needle-shaped crystals of the salt are precipitated on cooling), insoluble in ammonia.

(b) Sulphuric acid (H_2SO_4) throws down a heavy white precipitate of lead sulphate (PbSO_4), insoluble in acids, but soluble in caustic soda or in an ammoniacal solution of tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$).

(c) Potassium iodide (KI) precipitates yellow lead iodide (PbI_2), which is soluble in boiling water; on cooling, brilliant golden scales of the salt are precipitated.

On examining these reactions, we notice that lead chloride is soluble in hot water, whereas the other chlorides of the group are insoluble; further, that silver chloride is dissolved by ammonia, mercurous chloride remaining undissolved, but being blackened by this reagent. A method of separation is thus easily framed.

Separation of Group I.—To a solution containing the three metals add hydrochloric acid, collect the ensuing precipitate on a small filter, wash it once or twice with *cold* water, remove it to a test-tube, and boil it with water; filter while hot, and to the filtrate add sulphuric acid; a white

* As lead chloride is sparingly soluble in cold water, traces of the metal will be present in the filtrate, and may be detected by the methods given under the next group.

precipitate indicates LEAD (III. *b*). Pour a little conc. ammonia solution over that portion of the group precipitate which is insoluble in water : it is blackened, showing the presence of MERCURY (II. *a*). Acidulate the ammoniacal filtrate with nitric acid : a white precipitate tells you that SILVER is present (I. *a*).

SPECIAL REACTIONS FOR MEMBERS OF GROUP II.

I. MERCURY.*—Mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) is used.

1. *Dry Reactions*.—Same as those of mercurous compounds. (See p. 109.)

2. *Wet Reactions*.—Dissolve the salt in water and apply the following tests :—

(*a*) Sulphuretted hydrogen at first produces a white precipitate ($\text{HgS.Hg}_2\text{NO}_3$), which on the further addition of the reagent goes through a gradation of colours, black mercuric sulphide (HgS) being the last product. This precipitate is insoluble in ammonium sulphide, in hydrochloric or nitric acids, but is dissolved by boiling aqua regia.

(*b*) Stannous chloride produces at first a white precipitate of mercurous chloride, which changes, on addition of excess of the precipitant, to greyish-black metallic mercury.

(*c*) Copper foil—same as with mercurous salts (p. 109, II. *d*).

II. BISMUTH.—Bismuth chloride (BiCl_3) is used.

1. *Dry Reactions*.—On asbestos thread in reducing flame, a black metallic film, thin part brown, difficultly soluble in nitric acid. In oxidising flame, a yellowish-white oxide film. On charcoal splinter, yellow shining spiculæ, soluble in nitric acid.

2. *Wet Reactions*.—Dissolve in dilute hydrochloric acid, and test as follows :—

(*a*) Sulphuretted hydrogen throws down a brownish-

* There are two classes of mercury salts, the type of the first being calomel, Hg_2Cl_2 ; and that of the second corrosive sublimate, HgCl_2 . Distinct tests are given for each class.

black precipitate of bismuth sulphide (Bi_2S_3), insoluble in warm ammonium sulphide, but soluble in hot nitric acid.

(b) Ammonia throws down white bismuthous oxide (Bi_2O_3), which, collected on a small filter, washed, and dissolved in a *very little* hydrochloric acid (excess of acid being driven off by heat), again forms a solution of bismuth trichloride (BiCl_3), from which

(c) Water precipitates white insoluble bismuth oxychloride (*bismuthyl chloride* BiOCl), insoluble in tartaric acid. Compare VI. (c), p. 116.

III. COPPER.—Cupric sulphate (CuSO_4) is used.

1. *Dry Reactions*.—On charcoal splinter, red metallic bead, soluble in nitric acid; the solution gives a mahogany colouration with potassium ferrocyanide (best seen by sucking up a little of the liquid on to filter paper). With borax bead copper gives a blue glass; if a trace of a tin salt is added, and the bead heated in the lower reducing flame, the colour changes to red-brown, owing to the formation of cuprous oxide (Cu_2O). If this bead be alternately slowly oxidised and reduced, a ruby-red colour is obtained.

Small quantities of copper may be detected by bringing the substance to be tested, along with a little pure silver chloride made into a paste with water, supported on a thin iron wire, into the reducing flame, when a fine blue colour is imparted to the flame. (Gericke.)

2. *Wet Reactions*.—Dissolve the remaining crystals in water, and apply the following tests:—

(a) Sulphuretted hydrogen precipitates black cupric sulphide (CuS), nearly insoluble in ammonium sulphide and in hot dilute sulphuric acid, soluble in hot nitric acid.

(b) Ammonia, added drop by drop, produces a greenish-blue precipitate $2(\text{CuSO}_4 \cdot 2\text{CuO}) \cdot 5\text{H}_2\text{O}$ (Reindel), which disappears in excess of ammonia, a deep-blue liquid containing a double salt of ammonium and copper, $\text{CuSO}_4 \cdot 4\text{NH}_3$, being formed.

(c) Potassium ferrocyanide (K_4FeCy_6) produces a brown precipitate, or in very dilute solution a brown colouration, of copper ferrocyanide (Cu_2FeCy_6).

IV. CADMIUM.—Metallic cadmium is dissolved in nitric acid, the solution evaporated just to dryness, and the dry residue tested as follows :—

1. *Dry Reactions*.—On asbestos thread in reducing flame, a black film, thin part brown, instantly soluble in dilute nitric acid. Sulphide film lemon-coloured. On charcoal splinter, partly reduced, giving white ductile bead. Oxide film brown-black, passing through changes of colour till the outer part is reached, which is nearly white.

2. *Wet Reactions*.—Dissolve part of the residue—cadmium nitrate, $Cd(NO_3)_2$ —in water, and apply the following tests :—

(a) Sulphuretted hydrogen throws down yellow cadmium sulphide (CdS), insoluble in ammonium sulphide, also in potassium cyanide (*very poisonous*), but dissolved by hot dilute sulphuric acid, also by hot nitric acid.

(b) Ammonia precipitates white cadmium hydrate $Cd(OH)_2$, soluble in excess of the precipitant.

V. ARSENIC.—Arsenious oxide (As_2O_3) is used.

1. *Dry Reactions*.—On asbestos thread in reducing flame, black film, thin part brown, soluble in sodium hypochlorite, insoluble in dilute nitric acid. Sulphide film lemon-yellow, disappears when excess of ammonium sulphide is used, but reappears on breathing on the film. On asbestos thread in oxidising flame, white film with white fumes of arsenious oxide and pale lavender-blue flame. If this film be touched with a drop of ammonio-silver nitrate, it gives a yellow colour.

Heated in a bent tube (see p. 106), arsenious oxide sublimes and condenses on the cold part of the tube in octahedral crystals.

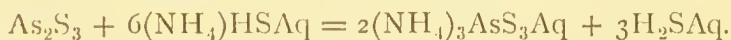
Heated in a tube closed at one end along with a fragment of charcoal (fig. 50), arsenious oxide is reduced, a mirror of metallic arsenic being formed on the cold part of the tube.



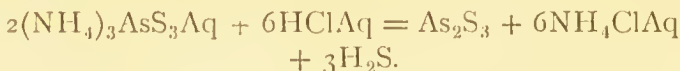
Heated in a closed tube with sodium acetate, cacodyl oxide, $\left\{ \begin{matrix} (\text{CH}_3)_2\text{As} \\ (\text{CH}_3)_2\text{As} \end{matrix} \right\} \text{O}$, is formed, recognisable by its strong garlic odour. *This substance is extremely poisonous.* Arsenic in presence of copper may be readily recognised by bringing the substance to be tested into the oxidising flame, and noticing the peculiar greyish-blue flame; then treating the residue with silver chloride, as directed on p. 112.

2. *Wet Reactions.*—Boil a little of the arsenious oxide in water, and to this solution apply the following tests:—

(a) Sulphuretted hydrogen, after addition of hydrochloric acid, precipitates the sulphide As_2S_3 , insoluble in concentrated hydrochloric acid, soluble in ammonium carbonate, and in ammonium sulphide with formation of a thio-arsenite:



On the addition of acid this salt is decomposed, arsenious sulphide being reprecipitated, thus:



(b) Ammonio-silver nitrate (*reagent list*) precipitates yellow silver arsenite (Ag_3AsO_3), soluble in excess of ammonia, also in nitric acid.

(c) Ammonio-cupric sulphate (*reagent list*) precipitates pale green copper-hydrogen-arsenite (CuHASO_3).

(d) Add a strong solution of caustic potash and a few pieces of metallic zinc, cover the mouth of the tube with paper moistened with silver nitrate, and very gently warm the tube. Arsenuretted hydrogen (AsH_3) is evolved, which is decomposed by the silver nitrate, a bluish-black stain of metallic silver being produced.

(e) Add a few drops of pure hydrochloric acid and a strip of bright copper foil, and boil the liquid. A lustrous brownish-black deposit (Cu_3As_2 , according to Lippert) is produced. The copper is removed, dried by pressing between folds of filtering paper, placed in a clean dry test-tube, and gently heated. The arsenic is volatilised and oxidised, and condenses on the colder part of the tube as arsenious oxide. The sublimate is dissolved in water, and tested with ammonio-silver nitrate and ammonio-copper sulphate (*vide supra*).

The hydrochloric acid used in this test must be free from sulphites or sulphurous acid, otherwise cuprous chloride is formed, which interferes with the subsequent reaction for arsenic.

Boil a small quantity of arsenious oxide in nitric acid; evaporate off the greater part of the acid, dilute with water, and test the solution of arsenic acid (H_3AsO_4) thus obtained, as follows :—

(f) After neutralisation with ammonia, silver nitrate throws down brick-red silver arsenate (Ag_3AsO_4), soluble in ammonia and nitric acid.

(g) Add excess of ammonia, then ammonium chloride and magnesium sulphate, a white precipitate of ammonium-magnesium arsenate, $(\text{NH}_4)\text{MgAsO}_4$, is produced.

VI. ANTIMONY.—Antimonious chloride (SbCl_3) is used.

1. *Dry Reactions*.—On asbestos thread, in reducing flame black metallic film, more lustrous and velvet-like than the arsenical film, insoluble in sodium hypochlorite. Sulphide film orange, disappearing when large excess of ammonium sulphide is used, but reappearing on blowing. Oxide film white; touched with ammonio-silver nitrate, and blown on with ammoniacal air, gives a black spot insoluble in ammonia.

On charcoal splinter yields white brittle metallic bead. In glass tube does not sublime.

Flame colouration pale greenish-blue, appearing greener on addition of silver chloride.

Dissolve part of the crystals in dilute hydrochloric acid and apply the following tests:—

(a) Sulphuretted hydrogen produces an orange-red precipitate of antimonious sulphide (Sb_2S_3), insoluble in ammonium carbonate, but dissolved by boiling concentrated hydrochloric acid, also by ammonium sulphide. See V. (a), p. 114.

(b) Ammonia throws down white antimony hydrate, $\text{Sb}(\text{OH})_3$.

(c) On the addition of water, white antimony oxychloride, *powder of algaroth* (SbOCl), is precipitated. This substance dissolves in tartaric acid. Compare II. (c), p. 112.

(d) Boil some of the solution of antimony chloride with a few drops of nitric acid for some time, then add, gradually, a *large excess* of solid ammonium carbonate, boil for some minutes, and filter; acidulate the filtrate with hydrochloric acid and add sulphuretted hydrogen: an orange-red precipitate (Sb_2S_3) shows that the whole of the antimony was not precipitated by the ammonium carbonate (*compare* reaction (f) for *tin*).

(e) Treated as directed in V. (d), p. 114, antimony compounds do not evolve antimonuretted hydrogen.

VII. TIN.—Stannous chloride (SnCl_2) is used—

1. *Dry Reactions*.—On charcoal splinter tin gives a white ductile bead, soluble in nitric acid, the solution giving a white precipitate with mercuric chloride. If a borax bead be coloured faintly blue by a copper salt, and a trace of a tin salt added, the colour of the bead changes to red when heated in the lower reducing flame.

2. *Wet Reactions*.—Dissolve some of the stannous chloride in dilute hydrochloric acid, and apply the following tests:—

(a) Sulphuretted hydrogen throws down dark-brown stannous sulphide (SnS) ; this precipitate is soluble in yellow (not in colourless) ammonium sulphide ; from this solution hydrochloric acid precipitates yellow stannic sulphide (SnS_2).

(b) Mercuric chloride throws down white mercurous chloride ; but upon addition of a further quantity of the stannous chloride solution, grey metallic mercury is formed.

Boil a portion of the stannous chloride solution with a few crystals of potassium chlorate for some minutes ; dilute the solution, and apply the following tests :

(c) Sulphuretted hydrogen gives a yellow precipitate of stannic sulphide, soluble in boiling concentrated hydrochloric acid, soluble in ammonium sulphide, insoluble in ammonium carbonate.

(d) Boiled with a large excess of water, stannic hydrate, $\text{SnO}(\text{HO})_2$, is precipitated.

(e) Add copper turnings, boil for some time (stannic is reduced to stannous chloride), pour off clear liquid and add mercuric chloride ; a grey precipitate is produced. See VII. (b), above.

(f) Add a *large excess* of solid ammonium carbonate, boil for some time and filter ; acidulate the filtrate and add sulphuretted hydrogen : no precipitate is produced ; the whole of the tin was precipitated (as SnO_2) by the ammonium carbonate. (Compare reaction (d) for *antimony*.)

Separation of Group II.—All the members of this group are precipitated by sulphuretted hydrogen ; but the sulphides of the three last-mentioned metals are soluble in ammonium sulphide, while those of the other metals are insoluble. The group is, therefore, divided into two sub-groups.

Further, sulphide of mercury is insoluble in nitric acid, whereas the other sulphides of Division I. are soluble.

Bismuth is precipitated by ammonia in excess, copper and cadmium are not.

By taking advantage of these and a few other properties of the members of the group, a method of separation may be readily framed.

After *thoroughly washing* the group precipitate produced by passing sulphuretted hydrogen gas through a *slightly* acid solution of the members of the group, transfer it to a small beaker or test-tube, add yellow ammonium sulphide and a little water. Set the beaker in a vessel containing water, and boil the water for 10 or 15 minutes; filter, preserve the filtrate (labelling it *Div. II.*). Wash the precipitate *thoroughly* with hot water, transfer it to a test-tube, and heat it with dilute nitric acid, filter from undissolved mercuric sulphide, wash thoroughly, and set aside the filtrate (labelled *Div. I., Cu, &c.*); dissolve the mercuric sulphide in aqua regia, boil off excess of acid, dilute with water, and test with stannous chloride for MERCURY (p. 109, II. (c)).

To filtrate *Div. I., Cu, &c.*, add ammonia in excess; filter off the ensuing precipitate of bismuth hydrate (test it further for BISMUTH by II. (b), p. 112); to the filtrate—which if blue shows the presence of COPPER—add potassium cyanide solution till the liquid is quite colourless, then pass in sulphuretted hydrogen; a yellow precipitate shows the presence of CADMIUM.

The solution labelled *Div. II.* is neutralised with hydrochloric acid, the ensuing precipitate collected, well washed, and *very gently* heated with a conc. solution of ammonium carbonate; the insoluble part is removed by filtration, and the filtrate acidified with hydrochloric acid; yellow arsenious sulphide is thrown down. Confirm ARSENIC by dry tests (see V. p. 113). The portion insoluble in ammonium carbonate is boiled with conc. hydrochloric acid and *two drops* of nitric acid, and a part is tested for ANTIMONY after removing tin by boiling with ammonium carbonate (VI. (d), p. 116); the remainder is tested for TIN by boiling with copper and then adding mercuric chloride (VII. (e), p. 117).

SPECIAL REACTIONS FOR THE MEMBERS OF GROUP III.

I. IRON.—(a) As ferrous salts. Ferrous sulphate (FeSO_4) is used.

1. *Dry Reactions*.—On charcoal splinter in reducing flame yields minute spiculæ, which are magnetic, soluble in hydrochloric acid, the solution giving a deep blue precipitate with potassium ferrocyanide. With borax bead in oxidising flame gives a yellowish brown ; in reducing flame, a bottle-green glass.

2. *Wet Reactions*.—Dissolve a few of the crystals in *cold* water, and apply the following tests :—

(a) Ammonia precipitates nearly white ferrous hydrate, $\text{Fe}(\text{HO})_2$, which absorbs oxygen from the air, rapidly changing its colour to green, and eventually being converted into reddish-brown ferric hydrate, $\text{Fe}(\text{HO})_3$.

(b) Ammonium sulphide throws down, after a little time if the solution be dilute, a black precipitate of ferrous sulphide (FeS), soluble in hydrochloric acid with evolution of sulphuretted hydrogen.

(c) Potassium ferrocyanide (K_4FeCy_6) produces a blue precipitate—Prussian blue ($\text{Fe}_7\text{Cy}_{18}$)—insoluble in acids, but decomposed by alkalis.

(d) Potassium ferricyanide (K_3FeCy_6) throws down a blue precipitate—Turnbull's blue ($\text{Fe}_5\text{Cy}_{12}$).

Boil a little of the ferrous sulphate solution with a few drops of conc. nitric acid until the liquid becomes of a yellow colour ; the iron is thus oxidised to the ferric state. From this solution—

(e) Ammonia at once throws down foxy-red ferric hydrate, $\text{Fe}_2(\text{OH})_6$.

(f) Sulphuretted hydrogen produces a precipitate of sulphur, while the ferric is reduced to a ferrous salt ; thus with ferric chloride :



(g) Add ammonia until the solution is exactly neutral, and then ammonium acetate, and boil the liquid ; a brownish-red precipitate, consisting of a mixture of basic ferric acetates, forms.

(h) Potassium ferrocyanide throws down Prussian blue. (See c.)

(i) Potassium ferricyanide produces no precipitate, but changes the colour of the solution to reddish brown.

(k) Potassium thiocyanate (KCNS), even in very dilute solutions, produces a blood-red colouration, due to the formation of soluble ferric thiocyanate, $\text{Fe}(\text{CNS})_3$.

(l) Barium carbonate suspended in water precipitates ferric hydrate mixed with basic salts, carbon dioxide being evolved.

II. ALUMINIUM. Alum is used for the tests.

1. *Dry Reactions.*—Compounds of this metal heated on platinum wire in the oxidising flame, moistened with cobaltic nitrate ($\text{Co}(\text{NO}_3)_2$), and again heated in the flame, give a deep-blue coloured mass. If the precipitate to be tested be very small, collect it on a minute filter, spread out the filter on a flat surface, cut away that portion on which there is no precipitate, place the filter containing the precipitate between the loops of the platinum wire (see p. 92, fig. 43, No. 3), gently dry the paper, incinerate it, moisten the ash with a drop of cobaltic nitrate solution from a capillary tube, and again heat in the oxidising flame.

The tests here given fail to detect aluminium compounds when present in such a substance as bread.

A part of the bread, in crumbs, is ignited in a platinum dish ; when the ash is white, or nearly so, it is warmed with a little pure hydrochloric acid, excess of acid being removed by heat. After cooling, a little piece of sodium, cut from the inside of a lump, is added, and then, very carefully, distilled water. When the sodium is completely oxidised

the contents of the basin are boiled, filtered, and ammonium chloride is added to the filtrate; if no precipitate appears after standing, alumina is absent. If a precipitate forms, it is collected on a very small filter, and tested as directed on p. 120.

2. *Wet Reactions.*

(a) Ammonia produces a white precipitate of aluminic hydrate, $\text{Al}_2(\text{HO})_6$.

(b) Ammonium sulphide produces the same precipitate.

(c) Caustic soda or potash throws down the same precipitate; it is soluble in an excess of the reagent, but reprecipitated by ammonium chloride.

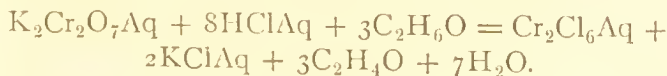
(d) Barium carbonate also precipitates aluminic hydrate mixed with basic salts.

III. CHROMIUM.—Potassium bichromate is used for the tests.

1. *Dry Reactions.*—Heated on platinum foil with potassium nitrate, a yellow mass of potassium chromate (K_2CrO_4), soluble in water, is formed.

On borax bead in oxidising and reducing flames, gives a green coloured bead.

2. *Wet Reactions.*—Dissolve a few crystals of potassium bichromate in water, add a little hydrochloric acid and alcohol, and boil until the liquid is dark green in colour. This solution now contains chromium chloride:



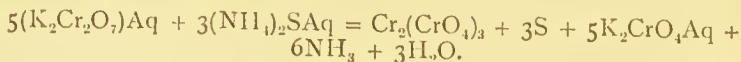
(a) Ammonia precipitates greyish-green chromic hydrate, $\text{Cr}_2(\text{OH})_6$.

(b) Caustic soda or potash produces the same precipitate. It is soluble in an excess of the precipitant, but is reprecipitated on boiling for a few minutes.

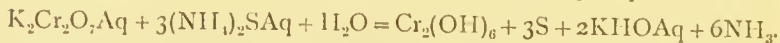
Chromium in certain compounds (the chromates) plays a chlorous rather than a basylous part. Its presence in such substances may be

detected as follows, using as example a solution of potassium dichromate in water.

(a) Ammonium sulphide throws down a brown precipitate consisting chiefly of chromium chromate, $\text{Cr}_2(\text{CrO}_4)_3$, the solution now containing potassium chromate, thus—



If ammonium sulphide be added in excess and the liquid boiled, green chromic hydrate, $\text{Cr}_2(\text{OH})_6$, mixed with sulphur, is precipitated—



(b) Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, precipitates yellow lead chromate, PbCrO_4 , soluble in caustic soda.

Manganese belongs to Group IV. ; but if present in a solution it is generally partially precipitated along with the members of Group III.

Separation of Group III.—Collect the precipitate produced by addition of ammonium chloride and ammonia, wash it thoroughly, dry and fuse it with potassium nitrate on platinum foil. Boil the fused mass* with water, filter, and to about one-fourth of the filtrate add acetic acid and lead acetate : a yellow precipitate, PbCrO_4 , shows the presence of CHROMIUM ; to the remainder of the filtrate add much ammonium chloride : a white jelly-like precipitate, $\text{Al}_2\text{H}_6\text{O}_6$, forming slowly, shows the presence of ALUMINIUM.

The insoluble part of the fused mass is dissolved in hydrochloric acid, and tested for IRON by potassium ferrocyanide (I. (c) p. 119).

SPECIAL REACTIONS FOR THE MEMBERS OF GROUP IV.

I. NICKEL.—Nickelous sulphate (NiSO_4) is used.

1. *Dry Reactions.*—On charcoal splinter nickel gives white ductile particles, which are slightly magnetic ; dissolved

* A bluish-green colour shows the presence of MANGANESE.

in nitric acid a green-coloured solution is produced, which on paper (p. 96) moistened with soda, exposed to bromine vapour, and again treated with soda, gives a black stain (Ni_2O_3). On borax bead in oxidising flame, gives a greyish-brown to red-brown glass; in upper reducing flame, grey (from reduced nickel).

2. *Wet Reactions.*—Make a solution of the salt in water, and apply the following tests:—

(a) Ammonium sulphide produces a black precipitate of nickelous sulphide (NiS), almost insoluble in cold dilute hydrochloric acid, soluble in aqua regia; the filtrate from this black precipitate is coloured deep brown, because some of the NiS oxidises in the air to NiSO_4 which dissolves; if the liquid is boiled *for some time* before collection of the NiS , the precipitate is rendered granular, and it does not then oxidise in the air.

(b) Caustic soda or potash precipitates light green nickelous hydrate, $\text{Ni}(\text{HO})_2$.

(c) Ammonia causes the formation of the same precipitate, soluble in an excess of the precipitant, forming a blue fluid from which nickelous hydrate is reprecipitated by caustic potash.

(d) Add a little acetic acid, then much potassium nitrite, and allow to stand; no precipitate is produced even after some hours. (*Compare reaction (d) for Cobalt.*)

II. COBALT.—Cobaltic nitrate ($\text{Co}(\text{NO}_3)_2$) is used.

1. *Dry Reactions.*—On charcoal splinter in reducing flame, white ductile particles, slightly magnetic, soluble in nitric acid, giving a reddish-coloured solution. Draw up a little of this solution on to filter paper and dry it; the colour changes to green.

In borax bead in either flame cobalt gives a bright blue glass. When heated in the upper reducing flame for some

time the bead becomes grey-coloured, owing to the separation of metallic cobalt.

2. *Wet Reactions*.—Dissolve a little of the salt in water, and apply the following tests :—

(a) Ammonium sulphide precipitates black cobaltous sulphide, CoS , insoluble in cold dilute hydrochloric acid, soluble in aqua regia.

(b) Caustic soda or potash precipitates a blue basic salt, which on boiling is converted into pink hydrate, $\text{Co}(\text{HO})_2$.*

(c) Ammonia produces the same precipitate ; it is soluble in an excess of the reagent, yielding a reddish-brown liquid.

(d) Potassium nitrite, added to a solution containing a little acetic acid, produces a yellow precipitate of cobalt-potassium nitrite ($\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$) ; the precipitate forms gradually. If a *large excess* of potassium nitrite is used, the liquid is thoroughly shaken, and is then allowed to stand for about an hour, the whole of the cobalt is precipitated as the double cobalt-potassium nitrite. (*Compare reaction (d) for nickel.*)

III. ZINC.—Zinc sulphate ($\text{ZnSO}_4 + 7\text{H}_2\text{O}$) is used.

1. *Dry Reactions*.—On asbestos thread, in reducing flame zinc gives a black metallic film, thin part brown.

In oxidising flame yields a white oxide film. Heated on platinum wire, moistened with cobaltic nitrate, and again heated, gives a green-coloured mass ; in applying this test for small quantities of zinc salts, use the method described under aluminium (p. 120).

2. *Wet Reactions*.—Dissolve the salt in water, and apply the tests as follows :—

(a) Ammonium sulphide precipitates white zinc sulphide (ZnS), soluble in mineral acids, insoluble in caustic potash or soda, and in acetic acid.

* Usually becomes more or less brown, owing to oxidation.

(b) Caustic potash or soda throws down white zinc hydrate, $\text{Zn}(\text{HO})_2$, soluble in excess of the precipitant ; the solution thus obtained is not reprecipitated by ammonium chloride.

IV. MANGANESE.—Manganese sulphate (MnSO_4) is used.

1. *Dry Reactions*.—On borax bead, in the oxidising flame manganese gives an amethyst-coloured glass, which becomes colourless in the reducing flame.

If a manganese compound be heated with sodium carbonate and a little potassium nitrate, a green bead is formed.

2. *Wet Reactions*.—Dissolve a little manganese sulphate in water, and apply the following tests to the solution :—

(a) Ammonium sulphide precipitates flesh-coloured manganous sulphide (MnS), soluble in acids (including acetic acid).

(b) Caustic potash or soda throws down a nearly white precipitate of manganous hydrate, $\text{Mn}(\text{HO})_2$, insoluble in an excess of the precipitant. By exposure to the air this hydrate is oxidised and darkens in colour. After such oxidation it is insoluble in ammonium chloride.*

(c) Treat a small quantity of the solution of any manganese salt (free from chlorine) with lead dioxide (PbO_2), add nitric acid (free from chlorine), and boil; the liquid assumes a reddish-purple colour, owing to the formation of permanganic acid (HMnO_4).

Separation of Group IV.—To a solution containing all the members of the group add ammonium sulphide in slight excess, *boil for ten minutes or so*, filter, and wash the precipitate with water containing a little ammonium sulphide to prevent oxidation of the sulphides. Remove the precipitate to a test-tube, shake it up with *dilute* hydrochloric acid, and filter. Boil the filtrate until all sulphuretted hydrogen is expelled, and then add caustic soda *in excess* ; a brown precipitate,

* This explains the fact that manganese is partly precipitated along with the members of Group III.

$\text{Mn}(\text{HO})_2$, shows presence of MANGANESE. Confirm by bead tests (see above). Again filter, and add ammonium sulphide to the filtrate ; a white precipitate (ZnS) shows presence of ZINC. That portion of the group precipitate which is insoluble in dilute hydrochloric acid is tested for COBALT by the borax bead (II., p. 123) ; the precipitate is then dissolved in a little hot conc. hydrochloric acid with a drop of nitric acid ; a slight excess of potash is added, and the liquid is then made acid by adding acetic acid ; this is followed by addition of a *large excess* of potassium nitrite (about a stick of the solid salt may be used), and the whole is shaken for some time and then set aside ; after an hour the liquid is filtered, and a little ammonium sulphide is added to the filtrate, which is then boiled until a black precipitate forms ; this precipitate is washed and tested in the borax bead for NICKEL (I., p. 123).

SPECIAL REACTIONS FOR THE MEMBERS OF GROUP V.

I. BARIUM. — Barium chloride (BaCl_2) is used.

1. *Dry Reactions*.—Supported on platinum wire, and heated in the zone of fusion, barium salts impart a green colour to the flame, appearing bluish-green when viewed through the green glass (see p. 101).

Certain barium salts, especially phosphates and silicates, must be moistened with hydrochloric or sulphuric acid before being brought into the flame.

2. *Wet Reactions*.—To a solution of the chloride in water add—

(a) Ammonia and ammonium carbonate ; a white precipitate of barium carbonate (BaCO_3) is thrown down.

(b) Potassium chromate, added after adding acetic acid, produces a yellow precipitate of barium chromate (BaCrO_4).

(c) Sulphuric acid precipitates barium sulphate as a heavy white powder.

(d) Ammonium oxalate throws down white barium oxalate (BaC_2O_4), soluble in hydrochloric and nitric acids.

II. STRONTIUM.—Strontium chloride is used.

1. *Dry Reactions*.—Strontium salts impart a crimson colour to the flame, appearing purple or rose when viewed through the blue glass.

2. *Wet Reactions*.—To an aqueous solution of the chloride apply the following tests :—

(a) Ammonia and ammonium carbonate precipitate white strontium carbonate (SrCO_3).

(b) Calcium sulphate solution produces a slight turbidity, but only after standing for some time (SrSO_4).

(c) A *little dilute* sulphuric acid precipitates white strontium sulphate on boiling

III. CALCIUM.—Calcium chloride is used.

1. *Dry Reactions*.—Calcium salts impart a yellowish-red colour to the flame, appearing greenish-grey when viewed through the blue glass.

On moistening a mixture of salts of the three metals barium, strontium, and calcium with sulphuric acid, carefully drying it, and bringing it, on a platinum wire, into the zone of fusion, the green colouration due to barium is at once visible. When this has disappeared, and when after moistening with hydrochloric acid no blue-green tint appears on viewing the flame through the green glass, the sample is again moistened with hydrochloric acid, and brought into the flame; while spirting it is examined through the blue glass for calcium (see III. above). After the greenish grey colour has disappeared, the rose-purple, which shows the presence of a strontium salt, is noticed. (Fresenius.)

2. *Wet Reactions*.—Dissolve the salt in water, and test the solution as follows :—

(a) Ammonium carbonate produces a white precipitate of calcium carbonate (CaCO_3).

(b) Calcium sulphate produces no precipitate.

(c) Much sulphuric acid precipitates calcium sulphate, but only from conc. solutions of calcium salts.

(d) Ammonium oxalate produces a white precipitate of

calcium oxalate (CaC_2O_4), soluble in hydrochloric and nitric acids ; insoluble in oxalic and acetic acids.

Separation of Group V.—Collect the precipitate produced by the addition of ammonium chloride, ammonia, and ammonium carbonate, wash it well, and dissolve a small part of it in dilute hydrochloric acid, and the rest in acetic acid. To the solution in hydrochloric acid add dilute sulphuric acid ; the immediate formation of a white precipitate shows BARIUM (I. (c), p. 126). To the solution in acetic acid add potassium chromate, and heat ; filter off the yellow precipitate (BaCrO_4), and to the filtrate add a *little very dilute* sulphuric acid, and boil ; collect the white precipitate that forms (SrSO_4 ; II. (c), p. 127), wash it well and examine it by the flame test for STRONTIUM (II. 1, p. 127). To the filtrate from strontium sulphate add ammonia in excess, then acetic acid till acid, and then ammonium oxalate ; collect and wash the white precipitate (CaC_2O_4), and examine it by the flame test for CALCIUM (III. 1, p. 127).

It may sometimes be necessary to test for the calcium group before precipitating the iron group. In such a case, sulphuric acid and a considerable volume of alcohol are added to the filtrate from the copper group, after boiling off all sulphuretted hydrogen. The precipitated sulphates are repeatedly washed with water, the washings are tested for calcium, and the residue for barium and strontium by the flame tests, as directed on p. 127.

SPECIAL REACTIONS FOR THE REMAINING METALS.

I. MAGNESIUM.—Magnesium sulphate ($\text{MgSO}_4 + 7\text{H}_2\text{O}$) is used.

2. *Wet Reactions.*—Dissolve the salt in water, and test the solution as follows :—

(a) Ammonium carbonate gives no precipitate.

(b) Ammonia precipitates white magnesium hydrate $\text{Mg}(\text{HO})_2$, soluble in ammonium chloride.

(c) Disodium-hydrogen phosphate (Na_2HPO_4), in presence of ammonia and ammonium chloride, precipitates white

crystalline magnesium-ammonium phosphate, $\text{Mg}(\text{NH}_4)\text{PO}_4$. In very dilute solutions the precipitation takes place only after some time, and is hastened by stirring the liquid with a glass rod. The presence of ammonium carbonate does not interfere with this reaction.

(*d*) Microcosmic salt, $\text{Na}(\text{NH}_4)\text{HPO}_4 + 4\text{H}_2\text{O}$, produces in hot solutions the same precipitate as in (*c*).

II. POTASSIUM.—Potassium nitrate (KNO_3) is used.

1. *Dry Reactions*.—A pale violet colour is imparted to the flame, appearing more crimson when viewed through the blue glass.

In the spectroscope potassium salts show two lines, one appearing in the outermost red, the other in the violet end of the spectrum. Sodium salts do not interfere with this reaction. (See Chart of Spectra.)

2. *Wet Reactions*.—Dissolve the salt in water, and test as follows :—

(*a*) Boil with conc. hydrochloric acid, concentrate and add platinum tetrachloride (PtCl_4) ; a yellow crystalline precipitate is formed ($\text{PtCl}_4 \cdot 2\text{KCl}$), insoluble in alcohol.

(*b*) Sodium-hydrogen tartrate ($\text{NaHC}_4\text{H}_4\text{O}_6$) precipitates, from conc. solutions, white potassium-hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$).

These precipitates (*a*) and (*b*) are more readily formed when the inside of the test-tube is rubbed with a glass rod.

III. SODIUM.—Common salt (NaCl) is used.

1. *Dry Reactions*.—Colours the flame intensely yellow. Viewed through the blue glass, the yellow rays are cut off ; hence if the flame caused by a mixture of sodium and potassium salts is viewed through the blue glass, the crimson-violet potassium flame is alone visible.

Viewed through the green glass, the sodium flame appears orange-yellow.

If a piece of paper coated with red mercuric iodide

is held close to the yellow sodium flame, the red colour appears changed to livid grey or fawn colour.

In the spectroscope sodium salts exhibit a distinct yellow line. (See chart of Spectra.)

2. *Wet Reactions*.—All the sodium salts with scarcely any exception are soluble in water; there is, therefore, no ordinary reagent which may be used to precipitate the compounds of this metal from their solutions.

IV. AMMONIUM.—(Hypothetical radicle, NH_4).

Dissolve a little ammonium chloride in water, and apply the following tests:—

(a) Platinum tetrachloride throws down yellow crystalline ammonium-platinic chloride ($2\text{NH}_4\text{Cl}.\text{PtCl}_4$), insoluble in alcohol.

(b) Sodium-hydrogen tartrate gives a white crystalline precipitate of ammonium-hydrogen tartrate ($\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$), soluble in a large quantity of water, and in ammonia.

(c) Nessler's solution gives a brown precipitate with solutions of ammonium salts; when these are present in *exceedingly minute* quantities, a brown colour only is formed.

(d) Caustic soda, or potash, heated with ammonium salts decomposes them, ammonia (NH_3) being evolved. (See Lesson VIII., p. 31.)

Separation of Group VI.—Heat a portion of the solution with caustic soda; AMMONIA is evolved.

Test in another part of the solution for MAGNESIUM by adding ammonia and sodium phosphate (see I. (c), p. 128).

Evaporate the rest of the solution to dryness, strongly heat the residue in a porcelain crucible until *all* the ammonium salts are volatilised, dissolve the residue in water, add a few crystals of pure oxalic acid, again evaporate to dryness, and heat strongly. On adding water and filtering, the magnesia remains in the insoluble portion as MgO ; the filtrate is evaporated to dryness and a portion tested for SODIUM by the flame test (see p. 129).

Dissolve the residue in water, and test for POTASSIUM by platinum tetrachloride (II. (a), p. 129), after boiling with a little conc. hydrochloric acid.

To illustrate the systematic application of the foregoing separations, we will take as example an actually occurring substance, viz. Fahl ore. This mineral may contain silver, mercury, lead, copper, bismuth, arsenic, antimony, iron, zinc, and sulphur, together with sand or gangue. Few specimens contain all these metals. A quantity of the mineral is reduced to fine powder by crushing in a steel mortar, and then pulverising it in an agate mortar. A portion of the sample is then treated in a small beaker glass with conc. nitric acid until the residue is white, or nearly so. During this process small particles of sulphur will probably separate and remain undissolved in the acid; these are yellow in colour, very porous, and generally float towards the surface of the liquid. After filtering from the sulphur and undissolved gangue, which is reserved for further examination, the nitric acid solution is evaporated to a small bulk, diluted with water, and hydrochloric acid added; the ensuing precipitate is collected (the filtrate being labelled F1. and preserved), washed, boiled in water, filtered, and the filtrate tested for lead by sulphuric acid (III. (b), p. 110). The portion insoluble in hot water is dissolved in ammonia, and to the solution nitric acid is added; a white precipitate is indicative of the presence of silver (I. (a) p. 108). The filtrate labelled F1. is boiled down until the greater part of the free acid is driven off, diluted with water, and saturated with sulphuretted hydrogen gas.

The precipitated sulphides of Group II. are collected on a filter (filtrate labelled F2.),* quickly washed with water containing a little sulphuretted hydrogen (to prevent oxidation of the sulphides), and gently warmed with a little yellow ammonium sulphide and water in the manner described on p. 118. Arsenic and antimony sulphides are thus dissolved.

* This filtrate must be again saturated with H_2S ; if any precipitate forms it must be added to the larger quantity.

The solution is separated from the residue, labelled F₃., and preserved. The residue, after being *thoroughly* washed with hot water until free from chlorine,* is boiled in nitric acid, the solution diluted and filtered (the filtrate labelled F₄.). The insoluble portion is dissolved in aqua regia, the liquid boiled down, diluted, and tested for mercury by means of stannous chloride (see I. (b), p. 111). To the filtrate F₄. a little dilute sulphuric acid (which must be free from lead) is added, the liquid is evaporated to a small bulk, allowed to cool, and mixed with water; if a white solid remains insoluble in the water it is lead sulphate (see p. 110). Confirm lead by reduction on charcoal splinter (pp. 95, 110).

Having filtered from the precipitated lead sulphate, add ammonia in excess; a blue colour shows the presence of copper. If a white precipitate forms, collect and wash it, dissolve it in one drop of hydrochloric acid, and add water; a turbidity insoluble in tartaric acid indicates bismuth (compare II. (c), p. 112).

The blue filtrate is mixed with potassium cyanide solution until the liquid becomes quite colourless, and the liquid is then tested for cadmium by means of sulphuretted hydrogen (p. 113).

The filtrate labelled F₃. is now acidified with hydrochloric acid, the precipitate which ensues is collected, well washed, very gently warmed with a conc. solution of ammonium carbonate, and the insoluble portion collected on a filter; the filtrate is acidified with hydrochloric acid, any yellow precipitate which may form is tested on the asbestos thread for arsenic (p. 99). The portion insoluble in ammonium carbonate, after being thoroughly washed, is dissolved by boiling in conc. hydrochloric acid with *one drop* of nitric acid; the solution is diluted, and a *large excess* of solid ammonium carbonate is added, little by little to prevent

* A small quantity of the washings, collected separately, is tested by adding one drop of nitric acid, boiling, and adding one drop of silver nitrate. If no white precipitate (AgCl) forms, the washing is complete.

spirting ; the liquid is then boiled for some minutes, and filtered if necessary, and the filtrate is acidulated by hydrochloric acid, and tested for antimony by sulphuretted hydrogen, which should produce an orange-red precipitate (see (d), p. 116). (Confirm by asbestos thread reaction, p. 99.)

The filtrate F2. contains the metals of Groups III. and IV. It is boiled until every trace of sulphuretted hydrogen is expelled ; that is, until a piece of bibulous paper moistened with lead acetate solution remains unchanged in colour when held over the boiling liquid. A few crystals of potassium chlorate are added, and the boiling continued until the fluid assumes a deep yellow colour. If any precipitate of sulphur at first forms, it disappears, being oxidised by this treatment with potassium chlorate.

Ammonium chloride and ammonia are now added, and the resulting precipitate collected and washed. A portion is dissolved in hydrochloric acid, and tested for iron by means of potassium ferrocyanide (I. (c), p. 119). Another portion is tested on the charcoal splinter for iron (p. 98). The filtrate from the precipitate by ammonia is mixed with a little ammonium sulphide ; if a white precipitate forms, it is probably zinc sulphide. Confirm by the flame reaction (III., p. 124).

The presence of sulphur was indicated when the ore was dissolved in nitric acid (p. 131). To confirm it, use the test with the charcoal splinter described on p. 98.

That portion of the ore which was found to be insoluble in nitric acid (see p. 131) is dried, removed to a porcelain crucible, and fused with about five times its weight of a mixture of sodium and potassium carbonates ; the fused mass is boiled in dilute hydrochloric acid, and the solution evaporated to dryness ; the residue is drenched with hydrochloric acid, hot water added, and the liquid filtered ; the insoluble part is tested for silver by the flame test (see p. 108). To the filtrate ammonia in excess is added. If any precipitate forms it is collected, washed, boiled in caustic

soda, the solution filtered, and ammonium chloride is added to the filtrate ; if a precipitate forms it is tested for alumina by the dry test, p. 120. The part insoluble in caustic soda is dissolved in hydrochloric acid, and tested for iron (I. (c), p. 119). The filtrate separated from the precipitate by ammonia (*vide supra*) is tested for calcium by adding ammonium oxalate (III. (d), p. 127). If any precipitate forms it is collected, and the filtrate tested for magnesium by means of sodium phosphate (see I. (c), p. 128).

B. REACTIONS OF THE INORGANIC ACIDS AND ACID RADICLES (INCLUDING OXALIC ACID).

I. SULPHURIC ACID (H_2SO_4) AND SULPHATES.—Use a solution of sodium sulphate in water.

(a) Barium chloride (BaCl_2) produces a white precipitate of barium sulphate (BaSO_4), insoluble in hydrochloric and nitric acids.*

(b) Sulphates are reduced to sulphides when heated on the charcoal splinter (see p. 98).

(c) Free sulphuric acid is distinguished from a sulphate by its charring action on cane sugar. A solution containing free sulphuric acid, when evaporated to dryness on a water bath with a few fragments of sugar, leaves a black charred residue

To detect very small quantities of free sulphuric acid, a few drops of a solution of cane sugar (1 part of sugar to 30 of water) are placed in a small porcelain basin, one drop of the suspected liquid added, and the basin heated on the water-bath ; a black stain is produced on the basin if the liquid contain so little as 1 part of free acid in 300 parts of water.

Small quantities of sulphur may be detected by heating the dry substance with a little piece of sodium in a hard glass tube, treating the residue with distilled water, and testing the solution—

* The presence of 'glacial phosphoric acid' or of sodium pyrophosphate dissolved in hydrochloric acid interferes with the barium chloride test for sulphuric acid ; the barium sulphate is only thrown down upon heating, and then appears as a semi-transparent flocculent precipitate. (Spiller.)

(1) With sodium nitro-prusside, when a violet colouration ensues.

(2) With ammonium molybdate dissolved in hydrochloric acid, when a blue colour is produced.

The presence of sulphur in a single hair may be detected by the latter test. (Schlossberger.)

II. HYDROFLUOSILICIC ACID (H_2SiF_6) AND SILICO-FLUORIDES.—For the preparation of this acid, see Lesson XVI., p. 59.

(a) Barium chloride precipitates white crystalline barium silico-fluoride (BaSiF_6).

(b) Potassium chloride produces a transparent gelatinous precipitate of potassium silico-fluoride (K_2SiF_6).

(c) Silico-fluorides, when warmed with concentrated sulphuric acid, evolve silicon fluoride, which etches glass (see p. 59).

III. PHOSPHORIC ACID (H_3PO_4) AND PHOSPHATES.—There are three modifications of this acid.

A. *Orthophosphoric Acid*.—Use a solution of disodium hydrogen phosphate (Na_2HPO_4) in water.

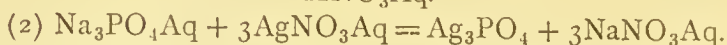
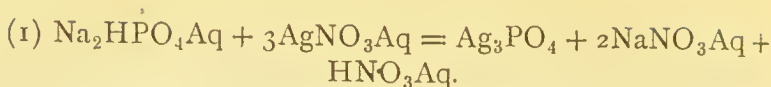
(a) Magnesium sulphate (MgSO_4), with previous addition of ammonium chloride and ammonia, throws down a white crystalline precipitate of magnesium-ammonium phosphate, $\text{Mg}(\text{NH}_4)\text{PO}_4$. Agitation of the liquid promotes the formation of this precipitate.

(b) Barium chloride produces a white precipitate of barium-hydrogen phosphate (BaHPO_4), soluble in nitric and hydrochloric acids.

(c) Silver nitrate throws down yellow silver phosphate (Ag_3PO_4), soluble in nitric acid and in ammonia. Filter off the liquid from the precipitated silver phosphate, and test it with litmus paper; its reaction is acid.

The liquid filtered from the same precipitate, when formed in a solution of trisodium phosphate, is neutral to test-paper if the whole of the phosphoric acid be precipitated.

In the first case nitric acid is produced; see next page:—



(d) One drop of hydrochloric acid is added, then sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) in excess, and finally *one or two drops* of ferric chloride (Fe_2Cl_6); a yellowish-white gelatinous precipitate of ferric phosphate (FePO_4) is formed. This precipitate is soluble in excess of ferric chloride, ferric acetate being formed.

(e) Ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$, in nitric acid on gently warming produces a yellow precipitate, consisting of molybdic acid with varying amounts of phosphoric acid and ammonia. This precipitate is soluble in ammonia, also in an excess of phosphoric acid or of a phosphate.

The presence of very minute quantities of phosphates may be detected by igniting the substance to be tested, crushing it to fine powder, placing a little of it in a small glass tube, about as thick as a straw, in which a little piece of sodium has been already placed, and gradually heating the tube to redness. Sodium phosphide is formed. After cooling, the fused mass is removed by breaking the tube, placed on a little piece of glass, and moistened with one drop of water, when the very characteristic odour of phosphoretted hydrogen (PH_3) is perceptible.

B. *Pyrophosphoric Acid*.—Heat a little sodium phosphate nearly to redness; cool, and dissolve in cold water.

From this solution, which contains sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$)—

(a) Silver nitrate precipitates white silver pyrophosphate ($\text{Ag}_4\text{P}_2\text{O}_7$), soluble in nitric acid, and also in ammonia.

(b) Albumen (white of egg) produces no precipitate.

C. *Metaphosphoric Acid*.—Heat to redness a quantity of ammonium-sodium-hydrogen phosphate, $(\text{NH}_4)\text{NaHPO}_4$, commonly called microcosmic salt; dissolve the residue in cold water, and to this solution of sodium metaphosphate (NaPO_3) add—

(a) Silver nitrate, which precipitates white silver metaphosphate (AgPO_3).

(b) Albumen, with the addition of acetic acid, is coagulated by this solution, a white flocculent precipitate being produced.

(For detection of phosphorus in organic compounds, see p. 188.)

IV. BORIC ACID (H_3BO_3) AND BORATES.—A solution of borax ($\text{Na}_2\text{B}_4\text{O}_7$) in water is used.

(a) Barium chloride precipitates white barium borate $\text{Ba}(\text{BO}_2)_2$, soluble in hydrochloric acid.

(b) Conc. sulphuric acid, when added to a hot concentrated solution of borax, causes a precipitate of boric acid.

(c) Acidulate with conc. sulphuric acid, add alcohol, and set fire to the mixture; the flame appears green, especially at the edges. The colour is best seen by repeatedly extinguishing and relighting the flame.

(d) Acidify with hydrochloric acid; immerse a strip of turmeric paper in the solution, withdraw and dry it; the paper acquires a characteristic brown tint. On moistening this paper with a solution of an alkali, the colour changes to bluish-black.

(e) Borates, when mixed with 1 part of fluor-spar (CaF_2) and 5 parts of potassium-hydrogen sulphate (KHSO_4), and the mixture heated on the platinum loop in the reducing flame of the Bunsen lamp, tinge the flame green. This is owing to the formation of volatile boron fluoride (BF_3); the green colour is visible only for a few seconds, and is best seen by viewing the flame against a black background.

By this test small quantities of boron may be detected in minerals. Two experiments should be made—one with the reagents alone, another after the addition of the substance to be tested.

V. OXALIC ACID ($\text{H}_2\text{C}_2\text{O}_4$) AND OXALATES.—A solution of ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, in water is used.

(a) Barium chloride precipitates white barium oxalate (BaC_2O_4), soluble in hydrochloric and nitric acids.

(b) Silver nitrate produces a white precipitate of silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$), soluble in nitric acid and in ammonia.

(c) Calcium chloride produces a white precipitate of calcium oxalate, insoluble in acetic acid.

This substance by gentle ignition is converted into calcium carbonate, which effervesces on the addition of an acid.

(d) On heating solid oxalates with conc. sulphuric acid, carbon monoxide and dioxide are evolved, and the residue is *not* blackened; the former gas burns with a pale lavender flame on bringing a light to the mouth of the tube; the presence of the latter is recognised by decanting the gaseous fumes into a test-tube containing clear lime-water. (See Lesson IX., p. 37.)

VI. HYDROFLUORIC ACID (HF) AND FLUORIDES.—(Fluorspar is used for the insoluble fluorides.)

(a) Barium chloride precipitates white barium fluoride (BaF_2), soluble in hydrochloric acid.

(b) Fluorides, when finely powdered, moistened with strong sulphuric acid, and *very gently* warmed in a leaden or platinum dish, evolve hydrofluoric acid. The capsule is covered with a watch-glass, having a thin film of wax spread over its convex side, letters being traced through the wax with a pin or other pointed instrument. Wherever the glass is exposed to the action of the hydrofluoric acid, it is etched; this etching is made apparent by removing the wax (by gentle warming) and breathing on the glass. (Compare Lesson XVI., p. 59.)

(c) Fluorides containing silica evolve silicon fluoride (SiF_4) when heated with sulphuric acid. If this gas be conducted through a wet glass tube, it is decomposed, hydrated silicic acid being deposited, which, on drying the tube, appears as a white powder on the glass.

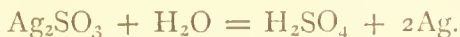
Small quantities of fluorine may be detected (1) by mixing the substance with a few drops of conc. sulphuric

acid in a watch-glass, heating until dry, and washing off the residue with water. A dull spot appears on the glass. Or (2) the substance (mixed with silica, if that body is not already present) is heated with strong sulphuric acid in a large test-tube, the evolved gas led into ammoniacal water in another tube, the liquid evaporated to dryness, the residue heated with water and filtered, the filtrate again evaporated to dryness, and the residue tested for fluorine as directed in (b) above. (Wilson.)

VII. SULPHUROUS ACID (H_2SO_3) AND SULPHITES.—A solution of sodium sulphite in water is used.

(a) Barium chloride precipitates white barium sulphite (BaSO_3), soluble in hydrochloric acid with evolution of sulphur dioxide.

(b) Silver nitrate throws down white silver sulphite (Ag_2SO_3). On heating, this precipitate becomes dark grey or black, metallic silver being produced :



(c) Treated with zinc and hydrochloric acid, sulphuretted hydrogen is produced : very small quantities of the acid may be thus detected. The zinc and acid employed must be pure ; a test with the reagents alone should precede the test for sulphurous acid.

(d) Free sulphurous acid (or sulphur dioxide in a gaseous mixture) may be detected by its power of liberating iodine from iodic acid. Paper moistened with starch paste containing a small quantity of this acid is rendered blue by the action of sulphurous acid.

(e) Acidulate with hydrochloric acid and pass sulphuretted hydrogen through the liquid ; sulphur is deposited, pentathionic acid, and other acids, being also produced.

VIII. SILICIC ACID— $\text{Si}(\text{HO})_4$ —AND SILICATES.

(a) The alkaline silicates are soluble in water ; their solutions are decomposed by acids, or by heating with ammonium chloride or carbonate, silicic acid separating as

a gelatinous precipitate. If the solution is very dilute it must be evaporated to dryness, when insoluble silicon dioxide (SiO_2) remains. This substance—

(b) When heated in the platinum loop with a *small quantity* of sodium carbonate yields a clear colourless bead, carbon dioxide escaping with effervescence. When heated with microcosmic salt the silica remains undissolved in the hot bead, forming the so-called silica skeleton bead.

For the purposes of analyses silicates may be divided into two classes—

(I.) Silicates decomposable by acids.

(II.) Silicates undecomposable by acids.

Silicates of the first class are analysed by evaporating the specimen, *reduced to very fine powder*, with hydrochloric acid, to complete dryness, adding dilute acid, and boiling with addition of water. On filtering, the insoluble silica remains on the filter (test in the bead before the Bunsen flame), while the bases may be detected in the filtrate.

Silicates of Class II. are *finely* powdered, and mixed in a platinum crucible with about five parts of a mixture of potassium and sodium carbonates. The mixture is fused over the blowpipe until a liquid mass is obtained, which after cooling, is boiled with hydrochloric acid, and subsequently evaporated to complete dryness; the remainder of the process is identical with that described above.

In order to detect the presence of alkalis in a silicate, the substance is fused with about three-fourths of its own weight of powdered ammonium chloride and three or four times its weight of pure calcium carbonate (prepared by dissolving marble in hydrochloric acid, adding milk of lime to alkaline reaction, filtering, and precipitating the filtrate, after heating, with ammonium carbonate). After fusion the mass is boiled with water for a considerable time, filtered, the lime precipitated by means of ammonium carbonate, and the filtrate from this precipitate evaporated to dryness, and the residue heated to expel ammonia. This residue is then

tested for sodium, potassium, and lithium. Fluorine may be detected by the method (c) on p. 138. Titanium by the method on p. 181.

IX. CARBONIC ACID (H_2CO_3) AND CARBONATES.—Sodium carbonate may be used.

(a) Barium chloride precipitates, from neutral solutions, barium carbonate (BaCO_3), soluble in acids with effervescence.

(b) Carbonates when pulverised and treated with hydrochloric acid evolve carbon dioxide (CO_2). If the gas resulting from the decomposition of a carbonate be decanted into a test-tube containing clear lime-water, a white precipitate of calcium carbonate is produced.

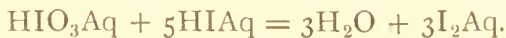
X. IODIC ACID (HIO_3) AND IODATES.—Use a solution of the acid in water.

(a) Barium chloride precipitates white barium iodate, $\text{Ba}(\text{IO}_3)_2$, soluble in nitric acid.

(b) Sulphur dioxide precipitates iodine; but when excess of the reagent is added, hydriodic acid is produced.



To detect iodates in the presence of iodides, acidulate the solution with sulphuric acid and add a little starch paste; if a blue colour is produced, an iodate is present (see VII. (d), p. 139).



XI. THIOSULPHURIC ACID ($\text{H}_2\text{S}_2\text{O}_3$) AND THIOSULPHATES.—Sodium thiosulphate is used.

(a) Hydrochloric acid, on gently warming, produces a precipitate of yellow sulphur, accompanied with the evolution of sulphur dioxide.

(b) Lead acetate produces a white precipitate of lead thiosulphate (PbS_2O_3). On boiling, this precipitate becomes black, being changed to a compound having the composition $\text{PbS.PbS}_2\text{O}_3 + \text{H}_2\text{O}$.

(c) Ferric chloride produces a reddish-violet colouration, which disappears on heating or on standing for some time.

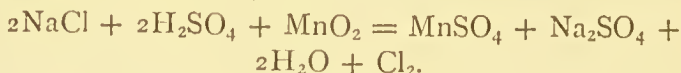
(*d*) Silver nitrate precipitates white silver thiosulphate ($\text{Ag}_2\text{S}_2\text{O}_3$), soluble in nitric acid. This precipitate rapidly blackens in colour, owing to the formation of silver sulphide (Ag_2S).

(For special reactions for Thionic Acids see p. 239).

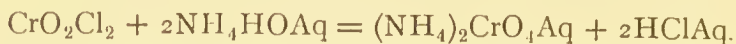
XII. HYDROCHLORIC ACID (HCl) AND CHLORIDES.—A solution of sodium chloride in water is used.

(*a*) Silver nitrate produces a white curdy precipitate of silver chloride (AgCl), which darkens on exposure to the light. This precipitate is insoluble in nitric acid, but dissolves easily in ammonia.

(*b*) Chlorides evolve chlorine when heated with sulphuric acid and manganese dioxide:



(*c*) Dry chlorides when heated in a dry retort with cone. sulphuric acid and potassium dichromate yield a dark red distillate of chromyl dichloride (CrO_2Cl_2), which on addition of ammonia gives a yellow solution containing ammonium chromate:



If a soluble lead salt be now added, a yellow precipitate of lead chromate (PbCrO_4) ensues; or a reddish colour is produced on adding an acid.

(*d*) If a little cupric oxide be dissolved in a bead of microcosmic salt in the oxidising flame, a small quantity of a chloride added, and the bead brought into the reducing flame, a bluish-coloured flame, inclining to purple, is seen around the bead. Viewed through the blue glass the flame appears azure blue inclining to green.

XIII. HYDROBROMIC ACID (HBr) AND BROMIDES.—A solution of potassium bromide in water is used.

(*a*) Silver nitrate precipitates nearly white silver bromide (AgBr), insoluble in dilute nitric acid; soluble in ammonia, potassium cyanide, or sodium thiosulphate.

(*b*) Bromides, when heated with sulphuric acid and

manganese dioxide, evolve bromine, which is recognised by its red colour, its smell, and by its power of turning starch paste yellow or yellowish red.

This test is best applied by gently heating the mixture in a small beaker, the mouth of which is covered with a watch-glass, to the lower side of which is attached a slip of paper moistened with starch paste and strewed over with dry starch. (Fresenius.)

(c) Dry bromides, when heated in a retort with conc. sulphuric acid and potassium bichromate, yield a dark red distillate, which consists of pure bromine. The addition of excess of ammonia to this liquid decolorises it completely.

This test serves to discriminate between bromides and chlorides, and also to detect either of these salts in presence of the other.

(d) Chlorine in the gaseous state or in solution decomposes solutions of bromides, bromine being liberated, and colouring the liquid more or less yellow. On shaking the tube after adding a few drops of carbon disulphide, the bromine is concentrated in this liquid, to which it imparts a reddish-brown colour. Excess of chlorine must be avoided, else the colour is discharged.

(e) Bromides treated as described for chlorides on p. 142 (d), give a blue flame, appearing greenish at the edges.

XIV. HYDRIODIC ACID (HI) AND IODIDES.—Potassium iodide is used.

(a) Silver nitrate precipitates pale yellow silver iodide (AgI), insoluble in dilute nitric acid, almost insoluble in ammonia, but easily dissolved by potassium cyanide or sodium thiosulphate.

(b) Bromine water liberates iodine from iodides; on shaking with carbon disulphide the iodine is concentrated in this liquid, forming a violet-coloured solution.

This appears to be the most delicate test for iodine. The bromine water should be rather dilute, a few drops are added, then a couple of drops of carbon disulphide, followed

by further *cautious* additions of bromine water, and *gentle* agitation of the liquid until the violet colouration is visible.

(c) A solution of nitrous fumes (*i.e.* N_2O_3 and NO_2) in conc. sulphuric acid likewise liberates iodine from iodides; chlorine water causes the same reaction. On the addition of a little starch paste a deep blue colour is produced, which disappears on heating the liquid. If an excess of chlorine water is used, no blue colour is produced on adding starch paste (owing to the formation of colourless iodine chloride); but if a reducing agent, as stannous chloride, be now added, the blue iodide of starch is re-formed.

(d) Copper sulphate, followed by excess of solution of sulphur dioxide, and boiling, precipitates cuprous iodide (Cu_2I_2).

(e) Boiled with ferric chloride, iodine is evolved:



(f) Dry iodides when heated in a glass tube closed at one end, with a little conc. sulphuric acid, evolve gaseous iodine, which fills the upper part of the tube, and is recognised by its violet colour.

(g) With the microcosmic bead, as directed for chlorides (p. 142 (d)), iodides give a green colouration to the flame.

Very small quantities of iodine may be detected by adding a little starch paste to the solution to be tested, a few drops of a dilute solution of potassium bichromate, just sufficient to communicate a pale yellow colour, and finally a drop or two of hydrochloric acid, when a blue colour, or, in extremely dilute solutions, a tawny colour, is apparent.

Chlorine, bromine, and iodine, in organic compounds are detected by heating the finely powdered substance with pure lime in a hard glass tube, dissolving the contents of the tube in dilute nitric acid, and applying the several tests to this solution. The substance, if a liquid, is placed in a little glass bulb, which is set inside the glass tube.

Iodides, bromides, and chlorides, when present together in a solution, may be detected as follows:—

The solution is divided into two portions. To the first portion a drop of a solution of nitrous fumes* in sulphuric acid is added, and then a few drops of carbon disulphide, with gentle agitation; the carbon disulphide assumes a violet colour more or less deep according to the quantity of IODINE present. The liquid is decanted, a drop or two of carbon disulphide again added, and then dilute chlorine water, drop by drop with gentle agitation. The characteristic reddish-yellow colour of BROMINE soon appears. The second portion of the solution is evaporated to dryness with addition of sodium carbonate, the dry mass fused with potassium bichromate in a porcelain crucible; if iodine is present, it is driven off. The fused mass is broken into little pieces, which are placed in a retort and heated with concentrated sulphuric acid. The distillate is divided into three parts. One part is treated with ammonia; if it assumes a yellow colour, chromyl dichloride is present. As a confirmatory test, the second part of the distillate is boiled with the addition of alcohol, and a little hydrochloric acid and ammonia added (see tests for chromium, p. 121). If a pale green precipitate forms, the presence of chromium is conclusively proved. CHLORINE was, therefore, present in the original mixture. (See XII. (c), p. 142.) The third part is mixed with water, and tested for bromine by agitation with ether or carbon bisulphide. Chlorine, in presence of iodine and bromine, may also be detected by acidulating the solution with a few drops of sulphuric acid, adding potassium permanganate solution until a slight permanent pink colour is produced, boiling for five or ten minutes, and testing with silver nitrate (p. 142).

XV. HYDROCYANIC ACID (HCN) AND CYANIDES.—A solution of potassium cyanide in water is used.

(a) Silver nitrate precipitates white silver cyanide (AgCN), insoluble in nitric acid, soluble in ammonia, also in excess of potassium cyanide and in sodium thiosulphate. Silver

* A solution, in conc. sulphuric acid, of the oxides of nitrogen produced by heating starch with HNO_3 .

cyanide is decomposed on ignition, metallic silver being produced. In this respect it differs from silver chloride.

(b) A solution containing a mixture of ferrous and ferric salts (prepared by adding a drop or two of ferric chloride to ferrous sulphate solution) throws down, from solutions of the cyanides made alkaline by caustic soda, a greenish-blue precipitate consisting of Prussian blue with admixed hydrated iron oxides. On the addition of hydrochloric acid the latter are dissolved, Prussian blue remaining.

(c) A few drops of hydrochloric acid are added to a little of the potassium cyanide solution in a small basin, which is covered with another basin to the convex side of which a drop of yellow ammonium sulphide adheres. The lower basin is very gently heated, the upper basin removed after a minute or two, and excess of ammonium sulphide driven off by *very slightly* warming the basin, and blowing on the drop of liquid. Ammonium sulphocyanide, $(\text{NH}_4)\text{CyS}$, is thus formed. When the basin is quite cool, add one drop of ferric chloride to the spot on the dish; a blood-red colouration is produced. (Compare (k), p. 120.)

Analysis of Cyanides.—All cyanides evolve hydrocyanic acid when heated with concentrated hydrochloric acid. The alkaline cyanides may be dissolved in water, and the foregoing tests applied. Mercuric cyanide (HgCy_2) is dissolved in water, the mercury removed as sulphide by precipitation with sulphuretted hydrogen, and the filtrate tested as above. The other simple cyanides may be fused in a porcelain crucible with sodium carbonate, the fused mass dissolved in water, and to this solution the usual tests applied.

The insoluble double cyanides (Prussian blue, Turnbull's blue, &c.) must be boiled with caustic soda and filtered. The precipitate contains the bases (ferric oxide, &c.), which are separated in the usual manner. Potassium ferro- or ferri-cyanide goes into solution along with the bases soluble in caustic soda which may be present (lead, zinc, or alumi-

nium oxides). Sulphuretted hydrogen is passed through the alkaline liquid to remove these metals, and the filtrate, after slightly acidifying with hydrochloric acid and boiling, divided into two parts, one of which is tested for potassium ferrocyanide with ferric chloride (see (*h*), p. 120), and the other for ferricyanide with ferrous sulphate (see (*d*), p. 119).

The alkalies which are present in certain insoluble cyanides may be detected by heating with three volumes of concentrated sulphuric acid and one volume of water, until excess of acid is driven off. The residue is dissolved in hydrochloric acid, the heavy metals which may be present removed, and the alkalies detected by the usual methods.

XVI. NITROUS ACID— HNO_2 —AND NITRITES.—Potassium nitrite, dissolved in water, is used.

(*a*) Silver nitrate precipitates white silver nitrite (AgNO_2), soluble in a large excess of water.

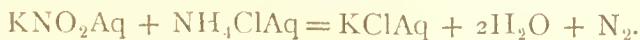
(*b*) Ferrous sulphate produces a brownish-black colouration, owing to the formation of nitric oxide, and its solution in the ferrous sulphate (compare reaction (*a*) under No. XIX.).

(*c*) Mercurous salts are reduced by nitrites, grey metallic mercury being deposited.

(*d*) Add a little potassium iodide, a drop of starch paste, and a few drops of dilute sulphuric acid; a blue colour ensues, owing to the decomposition of the potassium iodide, and the action of the liberated iodine on the starch.*



(*e*) Add a considerable quantity of ammonium chloride, boil till the mass becomes pasty, add water; the liquid is now free from nitrous acid:



(*f*) Add indigo solution and a few drops of dilute sulphuric acid; the colour of the indigo is *slowly* discharged.

* The potassium iodide used for this test must be free from iodate. If on addition of sulphuric acid and starch paste to the iodide, a blue colour is produced, it contains iodate (see reaction (*b*) for iodic acid, p. 141).

The reactions (b), (c), and (a) serve to distinguish between nitrites and nitrates.

XVII. HYPOCHLOROUS ACID— HClO —AND HYPOCHLORITES.—A solution of sodium hypochlorite in water is used.

(a) Silver nitrate produces a white precipitate of silver chloride.

(b) Lead nitrate throws down a precipitate which is at first white, but rapidly changes to red, and then to brown, from formation of lead dioxide (PbO_2).

(c) Manganese chloride (MnCl_2) precipitates dark brown hydrated manganese dioxide ($\text{MnO}(\text{HO})_2$).

(d) Add indigo solution and a few drops of dilute sulphuric acid; the colour of the indigo is *at once* discharged.

(e) Hypochlorites are decomposed by dilute hydrochloric acid with evolution of chlorine.

XVIII. SULPHYDRIC ACID— H_2S —AND SULPHIDES.—A solution of sodium sulphide is used.

(a) Silver nitrate precipitates black silver sulphide (Ag_2S).

(b) Solution of lead oxide in caustic soda throws down black lead sulphide (PbS).

(c) Sodium nitro-prusside ($\text{Na}_2\text{Fe}(\text{NO})\text{Cy}_5$) produces a deep but transient violet-red colour. This test is only applicable to sulphides of the alkali metals. Before applying it to other sulphides caustic soda or potash must be added to the solution to be tested.

(d) Most sulphides are decomposed by hydrochloric or sulphuric acid, sulphydric acid being liberated. This gas is recognised by its odour, and by its blackening action on paper moistened with a solution of a lead salt.

(e) When sulphides are fused on the platinum loop with a little solid caustic soda or potash, sodium or potassium sulphide is formed. These sulphides are soluble in water. If a silver coin be immersed in this solution it is blackened, owing to the formation of silver sulphide.

Sulphates are reduced to sulphides only by fusion in presence of reducing agents (see p. 98).

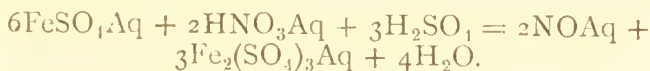
To detect sulphides in the presence of sulphates, sulphites and thiosulphates proceed as follows:—

A portion of the liquid is tested for SULPHYDRIC ACID by tests (c) and (d) above. Another portion is tested for SULPHURIC ACID by I. (a), p. 134. To a third portion of the solution, made alkaline by means of caustic potash, zinc sulphate solution is added in excess, the precipitate of zinc sulphide removed by filtration, and the filtrate divided into two portions. In one of these THIOSULPHURIC ACID is recognised by the evolution of sulphur dioxide, accompanied by the deposition of yellow sulphur, on warming with sulphuric acid. Another portion is *slightly* acidified with acetic acid, a small quantity of sodium nitroprusside solution is added, and then potassium ferrocyanide solution. A red colouration shows the presence of a SULPHITE.

(For the reactions of the Thionic Acids see Appendix.)

XIX. NITRIC ACID— HNO_3 —AND NITRATES.—Potassium nitrate (KNO_3) dissolved in water is used.

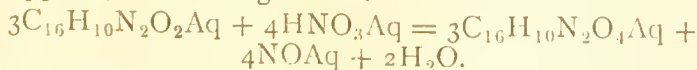
(a) Add a solution of ferrous sulphate, mix the liquids, and carefully pour a few drops of conc. sulphuric acid down the side of the test tube; a brown ring is formed at the point of contact of the two fluids.



(Compare Lesson V. p. 22.)

In applying this test to nitrates which are decomposed by sulphuric acid, giving rise to insoluble sulphates, e.g., barium nitrate, the solution is mixed with an equal volume of sulphuric acid, the precipitate allowed to settle, and a solution of ferrous sulphate then carefully added.

(b) Add a little indigo solution, a few drops of hydrochloric acid, and boil; the blue colour of the indigo disappears, *isatin* being formed.



(c) Add a little dilute sulphuric acid, a few drops of potassium iodide solution, and a little starch paste. Im-

merse a strip of zinc foil in the liquid, the nitric is reduced to nitrous acid, which liberates iodine from the potassium iodide (compare reaction (*d*) for nitrites, p. 147).

(*d*) Small quantities of nitric acid may be detected by evaporating the solution to dryness, moistening with a drop of *pure* sulphuric acid, and moving about a fragment of brucine in the liquid, when a rose-red colouration ensues. By using 1 c.c. of water this test will detect nitric acid in a water in which the quantity does not exceed .1 mgm. per litre (Nicholson).

To detect nitrates in the presence of chlorates the solution is poured into a little test-tube containing a few pieces of zinc foil, coated with spongy copper.* This tube is connected by means of a little bit of glass tubing with another smaller tube (see fig. 51). The second tube, *d*, serves to establish connection with the outer air.

The contents of the first tube are heated until the greater part of the liquid has distilled over into *a*. In this reaction hydrogen is produced, and by its action the nitric acid is reduced to ammonia ($\text{HNO}_3 + 8\text{H} = \text{NH}_3 + 3\text{H}_2\text{O}$). In the distillate ammonia is detected by its reaction with Nessler's solution (see test (*c*) for ammonia, p. 130).

The chlorate present is also reduced, a chloride being formed, which remains in solution in the first tube. On pouring off the liquid from this tube and testing it with silver nitrate, the reactions for chlorine are obtained (see p. 142). In the original solution the chloric acid may be detected by test (*a*) (*vide infra*).

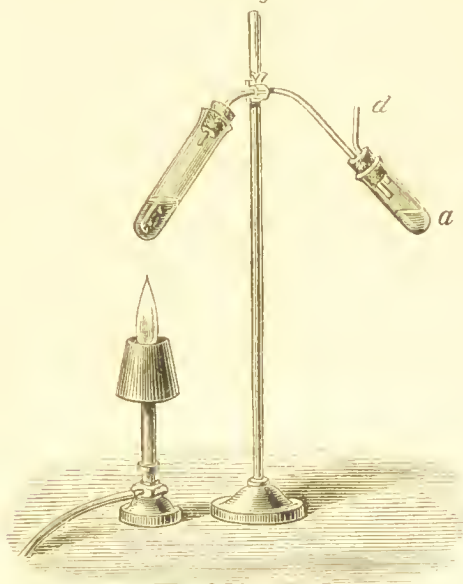
To detect nitrates in presence of iodides, add a mixture of copper and ferrous sulphates, (*a*) (p. 144), filter, and test the filtrate for nitric acid by (*a*) (p. 149). If iodides and bromides are present, add silver sulphate solution so long as

* A few pieces of zinc foil, cleaned by immersion in sulphuric acid and washing with distilled water, and bent so as to present a large surface in a small bulk, are placed in the test tube, and covered with a moderately warm solution of cupric sulphate; after the expiry of ten minutes or so the liquid is poured off, and the foil, which is now coated with spongy copper, carefully washed with distilled water.

a precipitate is formed, boil, filter, and test for nitric acid in the cooled filtrate.

Nitrogen in organic bodies may be detected by heating the substance in a clean dry test-tube, with a small piece of metallic potassium, whereby potassium cyanide is produced.

FIG. 51.



After cooling, water is carefully added, the solution filtered, and cyanogen detected by test (b) (p. 146).

XX. CHLORIC ACID— HClO_3 —AND CHLORATES.—A solution of potassium chlorate in water is used.

(a) A few drops of indigo solution are added, the liquid acidulated with sulphuric acid, and sulphurous acid (or sodium sulphite dissolved in water) added drop by drop. The blue colour is discharged.

(b) Dry chlorates treated with sulphuric acid evolve a yellow explosive gas (ClO_2). In applying this test only a small quantity of the salt must be used, and the mixture kept cold, otherwise a violent explosion may occur.

(c) Chlorates when heated evolve oxygen, a chloride being simultaneously formed.

(For detection of chlorates in the presence of nitrates, see p. 150.)

XXI. PERCHLORIC ACID — HClO_4 — AND PERCHLORATES.—Potassium chlorate is fused until the evolution of gas nearly ceases, and the mass gets semi-solid. The residue contains potassium perchlorate, which is separated from admixed chlorate and chloride by dissolving out the latter salts in successive small quantities of warm water, the perchlorate being much more insoluble than either of the other salts.

(a) Heated with conc. sulphuric acid, white fumes of hydrated perchloric acid are evolved.

(b) The solution of a perchlorate, mixed with hydrochloric acid, does not discharge the colour of indigo solution.

(c) Dry perchlorates when heated evolve oxygen.

C. REACTIONS OF THE ORGANIC ACIDS.

The organic acids are in general more difficult to detect than the inorganic acids. The tests here given serve, in most cases, for the identification of the more commonly occurring members of this group of acids.

The only organic acids which we shall notice are—

Tartaric, citric, benzoic, succinic, acetic, formic, ferrocyanic, ferricyanic, and thiocyanic acids.

I. TARTARIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$).—A solution of sodium or potassium tartrate in water is used.

(a) Solutions of the tartrates (if neutral, acidify with acetic acid) give a white precipitate of potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, on the addition of caustic potash.

(b) Calcium chloride in excess precipitates white calcium tartrate ($\text{CaC}_4\text{H}_4\text{O}_6$), soluble in acids, also in salts of ammonium. This precipitate, after being *thoroughly* washed, is soluble in *cold* caustic potash, but is reprecipitated on boiling.

(c) To a solution of a neutral tartrate add silver nitrate; filter off the white precipitate of silver tartrate ($\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$) which forms; dissolve this in the smallest possible quantity

of ammonia, and warm the solution for some time; a mirror of silver is formed on the test-tube.

II. CITRIC ACID ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$).—A solution of sodium citrate in water is to be used.

(a) Calcium chloride in excess produces, on boiling, a white precipitate of calcium citrate, $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$. This precipitate is *insoluble* in caustic potash, but soluble in hydrochloric acid. It is also soluble in solutions of ammonium salts.

(b) Lime-water produces a similar precipitate on boiling the liquid.

Tartaric acid in the presence of citric acid may be detected by adding hydrated ferric oxide to the solution, heating the mixture to about 90° , filtering from undissolved ferric oxide, and evaporating the filtrate to a syrupy consistence. If tartaric acid is present, an insoluble basic tartrate is formed and precipitated, ferric citrate remaining in solution.

III. BENZOIC ACID ($\text{HC}_7\text{H}_5\text{O}_2$).—The ammonium salt, dissolved in water, is used.

(a) Calcium chloride gives *no precipitate*.

(b) Ferric chloride precipitates (from neutral solutions) ferric benzoate, which is decomposed by ammonia, ferric hydrate remaining as an insoluble residue. This precipitate is decomposed by a small quantity of hydrochloric acid, benzoic acid being liberated.

(c) Hydrochloric acid produces a precipitate of free benzoic acid, very sparingly soluble in water.

IV. SUCCINIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_4$).—Ammonium succinate dissolved in water is used.

(a) Barium or calcium chloride alone gives no precipitate, but on the addition of alcohol, white barium or calcium succinate ($\text{Ba (or Ca) C}_4\text{H}_4\text{O}_4$) is precipitated.

(b) Ferric chloride gives a brownish-red precipitate of ferric succinate, which behaves like ferric benzoate with ammonia.

V. ACETIC ACID ($\text{HC}_2\text{H}_3\text{O}_2$).—A solution of sodium acetate in water is used.

(a) Ferric chloride in neutral solutions produces a deep blood-red colour. This solution, on addition of hydrochloric acid, turns yellow, and may be thus distinguished from ferric thiocyanate. On boiling the red solution, all the iron is precipitated as a basic acetate, the liquid becoming colourless, provided the iron be not in excess.

(b) Dry acetates, heated with arsenious oxide, yield the very foully-smelling poisonous cacodyl oxide $[\text{As}(\text{CH}_3)_2]_2\text{O}$.

(c) With silver nitrate a white precipitate of silver acetate ($\text{AgC}_2\text{H}_3\text{O}_2$) is formed in conc. solutions.

(d) Treated with conc. sulphuric acid and alcohol, the characteristic fruity smell of ethyl acetate ($\text{C}_2\text{H}_5\cdot\text{C}_2\text{H}_3\text{O}_2$) is perceived.

VI. FORMIC ACID (HCHO_2).—Sodium formate dissolved in water is used.

(a) With ferric chloride the formates behave like the acetates.

(b) Heated with silver nitrate, a precipitate of metallic silver is produced. Silver formate is first produced; this is then reduced to metallic silver ($2\text{AgCHO}_2 = 2\text{Ag} + \text{CO}_2 + \text{HCHO}_2$).

(c) Mercuric chloride on gently warming produces a white precipitate of mercurous chloride.

VII. FERROCYNANIC ACID — $\text{H}_4\text{FeC}_6\text{N}_6$ — AND FERROCYNANIDES.—A solution of potassium ferrocyanide is used.

(a) Silver nitrate precipitates white silver ferrocyanide ($\text{Ag}_4\text{FeC}_6\text{N}_6$), insoluble in nitric acid and in ammonia, but soluble in potassium cyanide.

(b) Ferric chloride produces a dark greenish-blue precipitate of ferric ferrocyanide, $\text{Fe}_4(\text{FeC}_6\text{N}_6)_3$ (Prussian blue), insoluble in dilute acids, but decomposed by caustic potash or soda, with separation of ferric hydrate and formation of an alkaline ferrocyanide.

(c) Ferrous sulphate throws down a white precipitate of ferrous ferrocyanide, which rapidly becomes blue owing to oxidation.

(d) Copper sulphate forms a brown precipitate of copper ferrocyanide, or in very dilute solutions only a brown colouration; boiling with sulphurous acid forms $\text{Cu}_4\text{FeC}_6\text{N}_6$.

VIII. FERRICYANIC ACID— $\text{H}_3\text{FeC}_6\text{N}_6$ —AND FERRICYANIDES.—A freshly-prepared solution of potassium ferri-cyanide is used.

(a) Silver nitrate precipitates orange-red silver ferri-cyanide ($\text{Ag}_3\text{FeC}_6\text{N}_6$), insoluble in nitric acid but soluble in ammonia.

(b) Ferric chloride produces no precipitate, but a reddish colouration.

(c) Ferrous sulphate produces a dark-blue precipitate of ferrous ferricyanide, $\text{Fe}_3(\text{FeC}_6\text{N}_6)_2$ (Turnbull's blue), insoluble in acids, but decomposed by caustic potash or soda.

(d) Copper sulphate precipitates yellow copper ferricyanide, $\text{Cu}_3(\text{FeC}_6\text{N}_6)_2$; boiling with sulphurous acid forms $\text{Cu}_4\text{FeC}_6\text{N}_6$.

IX. THIOCYANIC ACID— HCNS —AND THIOCYANATES.—A solution of potassium or ammonium thiocyanate is used.

(a) Silver nitrate throws down white silver thiocyanate, AgCNS , insoluble in nitric acid, but soluble in conc. ammonia and in potassium cyanide.

(b) Ferric chloride produces an intense blood-red colouration, due to the formation of ferric thiocyanate. The colour is not affected by hydrochloric acid, but is discharged on addition of mercuric chloride.

(c) Ferrous sulphate produces no change.

(d) Copper sulphate precipitates black cupric thiocyanate, $\text{Cu}(\text{CNS})_2$, which gradually changes to white cuprous thiocyanate, $\text{Cu}_2(\text{CNS})_2$. This change takes place at once in presence of a reducing agent such as ferrous sulphate or sulphurous acid.

D. SYNOPSIS OF ANALYTICAL METHODS.

TABLE A.

HEAT THE SOLID SUBSTANCE IN A GLASS TUBE CLOSED AT ONE END.

It Fuses. Alkaline salts Water of crystallisation	It does not Fuse, but changes Colour.	It evolves Gas.	It forms a Sublimate.	Drops of Water are formed.
It fuses, and changes colour. Colour white Hot Cold Bismuth oxide. } <i>yellow. dark yellow</i> Lead oxide. } <i>yellow. dark red</i>	Before heating. — Zinc oxide. } <i>white. yellow</i> Stannic oxide. } <i>straw. dark yellow</i> Ferric oxide. } <i>brown. black</i> Mercuric oxide. } <i>red. brown red</i>	1. Gases are colourless and odourless a. <i>Oxygen</i> . Easily decomposed peroxides, chlorates and nitrates. b. <i>Carbon monoxide</i> . Oxalates. 2. Gases are colourless, but possessed of an odour. a. <i>Ammonia</i> . Ammonium salts. b. <i>Sulphur dioxide</i> . Sulphites and certain sulphates. c. <i>Cyanogen</i> . Cyanogen compounds. 3. Gases are coloured. a. <i>Brown red</i> — N_2O_3 and N_2O_4 . Nitrites and certain nitrates of the heavy metals.	1. <i>Reddish brown drops</i> . Sulphur. 2. <i>White sublimate</i> . Ammonium salts, mercurous and mercuric chlorides, arsenious and antimonious oxides. 3. <i>Yellow sublimate</i> . Mercuric iodide, arsenious sulphide. 4. <i>Orange yellow sublimate, changing to black on heating</i> . Mercuric sulphide. 5. <i>Metallic mirror</i> . Arsenic. 6. <i>Metallic globules</i> . Mercury.	1. <i>Water of crystallisation, reaction generally neutral</i> . Easily fusible salts. 2. <i>Water of combination</i> . Generally non-fusible salts. a. <i>Water reacts acid</i> . Sulphites, chlorides, &c. b. <i>Water reacts alkaline</i> . Ammonium salts.
If the substance blackens, organic matter is present.				

This Table is to be used only as a guide to further Examinations. The reactions herein given may be masked by the presence of a number of metals; therefore, although we may not obtain a distinct reaction for a certain metal, we are not positively to decide that this metal is absent.

TABLE B.
FLAME REACTIONS WITH THE BUNSEN LAMP.
(Refer to page 90.)

A	B	C	D
Heated in the cold portion of the flame. The flame is coloured.	Heated on borax bead in the lower oxidising flame. The bead is coloured.	Heated on match splinter, in upper reducing flame, &c. Reduced metal is obtained.	Heated on asbestos in upper reducing flame, films are obtained on porcelain.
1. <i>Yellow</i> . . . Sodium	1. <i>Yellow</i> . Silver (often opal colour).	1. <i>Magnetic</i> . Iron. Nickel.	1. <i>Metallic-looking spots</i> . Probably Arsenic. Sulphide film yellow.
2. <i>Red</i> . . . { Strontium and Lithium	Bismuth (colourless when cold). Lead. Cadmium (only when present in large quantity, colourless when cold).	2. <i>Malleable</i> . (Press the globules with the small pestle.) Lead, Tin, Silver, Copper (red colour).	2. <i>Sooty-like spots</i> . Antimony. S. F. orange.
3. <i>Green</i> . . . { Barium (Thallium)	Uranium (yellow green) { Chromium (emerald green). (blue when cold). Copper (cold).	3. <i>Brittle</i> . Antimony, Bismuth.	3. <i>Metallic mirror spreading over the disc</i> . Mercury. Iodide film yellow-red.
4. <i>Bluish green</i> . Copper	2. <i>Green</i> . {	(Further tests may be applied by dissolving the reduced metal and applying wet reactions, as described on p. 96.)	4. <i>Black film</i> . a. Lead . . . S. F. brownish red to black.
5. <i>Lavender</i> . . . Potassium	3. <i>Blue</i> . Cobalt.	4. Sulphates are thus reduced to sulphides. The reduced mass is to be treated with water, and a silver coin dipped into the solution, a <i>black stain</i> of Silver sulphide (Ag_2S) is noticed on the coin.	b. Cadmium S. F. lemon.
6. <i>Yellowish red</i> Calcium	4. <i>Red to Brown</i> . Nickel (nearly colourless when cold).		c. Zinc . . . " white.
	5. <i>Ametkyst</i> . Manganese.		d. Tin . . . " brown-yellow.

The use of this Table will afford valuable indication as to what metals we are likely to find, but further tests are necessary before deciding if a given metal is or is not present.

TABLE C.
SOLUTION OF THE SUBSTANCE.

A. <i>Metals and Alloys.</i>	B. <i>Substances which are neither Metals nor Alloys, and contain no Organic Matter.</i>	C. <i>Substances which are neither Metals nor Alloys, but contain Organic Matter.</i>
<p>Boil with conc. nitric acid. Dilute solution with hot water, and filter. (Examine solution after Table D.) Residue (if any) may be</p> <p>I. METALLIC: <i>Gold</i> or <i>Platinum</i>. Boil in aqua regia and evaporate with hydrochloric acid. Divide the solution into two portions and add to Portion <i>a</i>. Ferrous sulphate, precipitate <i>Gold</i>. Portion <i>b</i>. Potassium chloride, precipitate <i>Platinum</i>.</p> <p>II. WHITE and NON-METALLIC: <i>Tin</i> or <i>Antimony</i> (as oxides). Wash well. Boil with concentrated tartaric acid solution. <i>a</i>. Everything dissolves. <i>Antimony</i>. (Solution gives orange precipitate with sulphuretted hydrogen). <i>b</i>. An insoluble substance remains. <i>Tin</i>. Confirm by match-reaction in Bunsen flame.</p>	<p>E. Boil a small quantity in fine powder with water. <i>a</i>. <i>All is dissolved</i>. Treat more of the substance with water, and examine solution after Table D. <i>b</i>. <i>An insoluble portion remains</i>. Filter; evaporate a few drops of filtrate on platinum foil. If there is a considerable residue, treat all the substance with water and proceed with filtrate by Table D; if only slight residue, proceed to next test.</p> <p>II. Part of that which was insoluble in water—or, if the substance was entirely insoluble in water, part of the original substance—is boiled with concentrated hydrochloric acid. (Notice if any gases are evolved.) <i>a</i>. <i>All is dissolved</i>. Treat more of original substance with hydrochloric acid; and, if blow-pipe test has shown no silicic acid, examine solution by Table D. If silicic acid be present, evaporate to dryness; warm residue with concentrated hydrochloric acid, dilute with water, filter from silica, and proceed by Table D. <i>b</i>. <i>Insoluble matter remains</i>. Dilute with water and boil again; if anything insoluble still remains, proceed to III.</p> <p>III. Another part of that which was insoluble in water—or, if it is completely insoluble therein, a portion of the original substance—is boiled with concentrated nitric acid. <i>a</i>. <i>All is dissolved</i>. Treat more of original substance in same way; evaporate to dryness, if necessary, to get rid of silicic acid, and proceed with solution by Table D. <i>b</i>. <i>Insoluble remains</i>. Boil this in aqua regia; if it dissolves, proceed with solution as in III. <i>a</i>; if insoluble, pass to Table N.</p>	<p>The organic matter must be removed, either by treatment with water, by ignition, or by gently warming with concentrated hydrochloric acid, with addition from time to time of potassium chlorate. The particular method to be employed will depend upon the nature of the material under examination.</p> <p>Compound cyanides are most easily decomposed by heating with concentrated sulphuric acid, and then boiling until the greater part of the acid is driven off.</p>

TABLE D.
TREATMENT OF THE SOLUTION.

A	B	C
<p><i>Treatment of the aqueous solution.</i></p> <p>Proceed with the systematic addition of the group reagents.</p>	<p><i>Treatment of the hydrochloric acid solution.</i></p> <p>Boil down to small bulk (about 30 c.c.); add a few drops of concentrated HCl, again boil down and now add water; if a white precipitate remain,* filter it off and examine it by Table E, and proceed with addition of group reagents to the filtrate, beginning with H₂S.</p>	<p><i>Treatment of the nitric acid solution.</i></p> <p>Evaporate the solution nearly to dryness, add HCl, again evaporate, and add water. If you have both a hydrochloric and a nitric acid solution, mix them together and evaporate almost to dryness; then add HCl and again evaporate; add water, and proceed with the addition of the group reagents, commencing with sulphuretted hydrogen. If silver, lead, or mercury be present in the nitric acid solution, the chlorides of these metals will remain undissolved on treatment with water: the insoluble portion must be treated as directed in Table E.</p>

* If this precipitate is amorphous and settles slowly, Bi, Sb, or Sn may be present; add a few drops of HCl to dissolve this precipitate, warm, and pass H₂S into the liquid.

TABLE E.
EXAMINATION OF PRECIPITATE BY HYDROCHLORIC ACID.

This Precipitate may be obtained on addition of Hydrochloric Acid to an aqueous solution, or sometimes to a Nitric Acid solution.

The precipitate, after being washed with cold water, is transferred to a test tube, boiled with water and filtered.

Solution. Add sulphuric acid
white precipitate = PbSO_4
LEAD.

(Confirm by flame reaction
Table B. C_2)

Residue. Treat
with ammonia and filter

Solution. Add nitric acid
white precipitate = AgCl
SILVER.

(Confirm B. C_2 .)

Insoluble portion.
Blackened = $\text{NH}_2\text{Hg}_2\text{Cl}$
MERCURY (as mercurous
salt).

(Confirm B. D_3 .)

If the original substance be a liquid, its action upon litmus-paper must be determined. If *acid*, the addition of *water* may precipitate basic bismuth and antimony salts. (Reserve for exam. by Table F.) If the solution be *neutral*, antimony sulphide— Sb_2S_3 —might be precipitated on addition of HCl , *e.g.* from a solution of Na_3SbS_4 in water, sulphuretted hydrogen being evolved (see Table F). Aqueous solutions of certain double cyanides are also decomposed by hydrochloric acid; hydrocyanic acid being evolved, and insoluble cyanides precipitated. (See Analysis of Cyanides, page 146.)

If the solution be *alkaline*, *hydrochloric acid* may precipitate arsenious or stannic sulphides (As_2S_3 , or SnS_2). Note the *colour* of the precipitate.

Silicic acid might also be precipitated from an alkaline solution. This precipitate will be *gelatinous*.

TABLE F.

EXAMINATION OF PRECIPITATE BY SULPHURETTED HYDROGEN.*

The Precipitate, after being *thoroughly* washed with water containing a few drops of sulphuretted hydrogen water, is warmed gently with ammonium sulphide (see p. 118) and filtered.

A. RESIDUE INSOLUBLE IN AMMONIUM SULPHIDE.	B. PORTION SOLUBLE IN AMMONIUM SULPHIDE.
<p>I Boil with dilute nitric acid.†</p> <p><i>a. Insoluble portion.</i> Dissolve in aqua regia, dilute, and add stannous chloride, white precipitate turning grey owing to the passage of HgCl to Hg. MERCURY, as <i>mercuric salt</i>. (Confirm by flame reaction.)</p> <p><i>b. Solution.</i> Add dilute sulphuric acid, and evaporate to small bulk; white residue insoluble in dilute HCl = PbSO₄. LEAD. (Confirm.)</p> <p>Filter, add ammonia; white precipitate = Bi(HO)₃. BISMUTH. (Confirm by (f) and (c), page 112.) Filter; a blue filtrate shows presence of COPPER. (Confirm by (c), page 113.)</p> <p>Add KCN until the solution is colourless, and then add a few drops of sulphuretted hydrogen water; yellow precipitate = CdS. CADMIUM.‡</p>	<p>Acidulate with hydrochloric acid. Collect and wash precipitate. § Treat with ammonium carbonate solution (see (a), page 114). Filter.</p> <p><i>Solution.</i> Acidulate with hydrochloric acid. Yellow precipitate = As₂S₃. ARSENIC. (Confirm by dry reactions, p. 114.)</p> <p><i>Insoluble part.</i> Dissolve in hot concentrated HCl, divide into two parts, test the larger part for Sn by copper test (p. 117); other part for Sb by adding a <i>large excess</i> of (NH₄)₂CO₃ (best added solid, a little at a time), boiling for a few minutes, filtering off SnO₂, acidulating filtrate with HClAq, and passing in H₂S (see p. 116).</p>

* When the precipitate by H₂S has been filtered off, H₂S must be again passed through the filtrate until the liquid smells strongly of the gas. The liquid is then warmed; any precipitate which may form must be added to the larger quantity. If a strong nitric acid solution is treated with sulphuretted hydrogen, this gas is decomposed, sulphur being thrown down. Nitric acid must therefore be removed by evaporation with HCl (p. 159) before adding the group reagent.

† Before adding nitric acid, make sure that the precipitate is *thoroughly* washed.

‡ Certain members of the next group yield precipitates with sulphuretted hydrogen; they are Fe₂O₃ and CrO₃; the precipitate is *white*, being merely sulphur; Fe₂O₃ is reduced to FeO, CrO₃ to Cr₂O₃, the solution turning *green*.

§ If this precipitate is *white*, it contains only sulphur formed by the decomposition of ammonium sulphide by hydrochloric acid.

TABLE G.

EXAMINATION OF PRECIPITATE BY AMMONIA IN PRESENCE OF AMMONIUM CHLORIDE.*

This precipitate may contain Manganese in addition to the members of the group proper. It may also contain certain salts, as phosphates, oxalates, &c., which are held in solution by a free acid, but on the addition of Ammonia are precipitated unchanged. Two cases are thus presented.

A. *Aluminium, Iron, Chromium, and Manganese only are present.*

Precipitate is *well* washed, fused with potassium nitrate and a little sodium carbonate, a green mass shows Mn; fused mass is boiled in water, a little alcohol added if Mn is present, and filtered: a *residue* is dissolved in hydrochloric acid, and potassium ferrocyanide added. Blue precipitate = Fe_3Cy_2 . IRON.

Filtrate. To about a fourth part add acetic acid and lead acetate, yellow precipitate shows CHROMIUM: to remainder of filtrate add ammonium chloride and allow to stand; white gelatinous precipitate forming slowly shows ALUMINIUM.

B. *Phosphates or Oxalates of the Alkaline Earths are also present.*

Test a part (about one-fourth) of the group precipitate for *Aluminium, etc.*, as directed under A.

Boil another small part of the precipitate with excess of sodium carbonate, filter, acidulate with acetic acid, and add calcium chloride. White precipitate shows OXALIC ACID.

Oxalates are present. Group precipitate is dried and strongly heated (to decompose oxalic acid), and residue dissolved in hydrochloric acid, ammonia added in excess, and precipitated with ammonium sulphide. (The filtrate from this precipitate contains the earths formerly combined with oxalic acid. Test for them according to Table I.)

This precipitate, or in case of oxalates being absent, the original group precipitate, is dissolved in hydrochloric acid, and the solution boiled with potassium chlorate. In a small portion, IRON is tested for with potassium ferrocyanide; in another small portion, PHOSPHORIC ACID is tested for with ammonium molybdate. The remainder of the solution is exactly neutralised with ammonia, boiled with ammonium acetate (if no reddening of the liquid ensues, add a few drops of ferric chloride) and filtered, and the filtrate tested for manganese, alkaline earths, and magnesia.

* Before adding these group reagents, expel *all* sulphuretted hydrogen from the liquid by continued boiling for 5 or 10 minutes, then add a little nitric acid and boil again to oxidise the ferrous salts which may be present.

TABLE H.
EXAMINATION OF PRECIPITATE BY AMMONIUM SULPHIDE.

Precipitate is washed with water containing a little Ammonium Sulphide, and then once with water alone.*
Treat the precipitate with *cold dilute* Hydrochloric Acid—filter.

A. *Residue.*

Test for COBALT in borax bead. (Table B.)
Dissolve in a few drops of hydrochloric acid (concd.) with addition of one crystal of potassium chlorate, evaporate to small bulk, dilute, add slight excess of caustic potash, then acetic acid till acid, then a *large excess* of potassium nitrite, shake, and allow to stand for at least an hour; filter off $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$, to filtrate add ammonium sulphide, boil, and examine black precipitate (NiS) for NICKEL by borax bead (p. 123).

B. *Filtrate.*

Boil so long as sulphuretted hydrogen is evolved (filter if necessary). Add excess of caustic potash. Precipitate = $\text{Mn}(\text{HO})_2$, changing to Mn_2O_3 . MANGANESE: confirm by sodium carbonate or borax bead (p. 125).

Filter, and to filtrate add ammonium sulphide. White precipitate = ZnS , ZINC: confirm by flame test (p. 124).

* Before filtering, boil for ten or fifteen minutes: the filtrate should be perfectly clear and colourless.

TABLE I.
EXAMINATION OF PRECIPITATE BY AMMONIUM CARBONATE IN PRESENCE OF
AMMONIUM CHLORIDE.*

Wash with hot water ; dissolve a small part in dilute Hydrochloric Acid, and the rest of the group precipitate in Acetic Acid.

A. *Solution in Hydrochloric Acid.*

Add a little dilute sulphuric acid, a white precipitate produced at once (BaSO_4) shows BARIUM.

(Confirm by flame reaction, see p. 126.)

B. *Solution in Acetic Acid.*

Add potassium chromate, heat, and filter from yellow BaCrO_4 ; to filtrate add a *little very dilute* sulphuric acid and boil for some time, a white precipitate (SrSO_4) shows STRONTIUM; confirm by flame reaction (see p. 127); make the filtrate from SrSO_4 slightly alkaline by ammonia, then acid by acetic acid, and add ammonium oxalate, a white precipitate (CaC_2O_4) shows CALCIUM.

(Confirm by flame reaction, see p. 127.)

To a *part* of the filtrate from the *group precipitate* add sodium phosphate, and agitate briskly. White Precipitate = $\text{Mg}(\text{NH}_4)\text{PO}_4$. MAGNESIUM.†

* The solution to which the group precipitant is added must be very gently warmed, not boiled.
† If a white *flocculent* precipitate forms, it may contain traces of aluminium phosphate or calcium phosphate.

TABLE K.
EXAMINATION FOR SODIUM, POTASSIUM, AND AMMONIUM.

A. *Ammonium*.

The original substance or solution is heated with caustic potash. Ammonia is thus evolved, recognisable by its smell, by its forming white fumes with hydrochloric acid, and by its action on red litmus paper. (See IV, (d') p. 130.)

B. *Potassium and Sodium*.

The remainder of the solution in which magnesium has been detected is evaporated to dryness, and strongly heated in a small crucible to get rid of ammonium salts. The residue is dissolved in water, a few crystals of pure oxalic acid added, again evaporated to dryness, and the residue again strongly heated (the alkalis are thus converted into carbonates), water is added, the solution filtered, and the filtrate evaporated to dryness. Part of the residue is tested in the flame for sodium (p. 129); the remainder is dissolved in a few drops of water, and tested for potassium by means of platinum tetrachloride (p. 129).

If magnesium be absent, the residue, after heating to expel ammonium salts, is at once tested for sodium and potassium.

TABLE L.

PRELIMINARY EXAMINATION FOR THE ACIDS.

When the base has been discovered, refer to the Table of Solubilities. If the substance is soluble in water, certain acids are excluded, because their compounds with the base present are insoluble in water. Some idea as to the acid present is thus obtained.

Heat a little of the substance with two or three times its volume of conc. Sulphuric Acid.

A. No action ensues.		B. Vapours are evolved.	
<i>Silicic, boric, phosphoric, sulphuric, iodic, arsenic,* titanio acids.</i>			
a. Coloured Gases.		b. Colourless Gases.	
<i>Hydriodic</i> . . .	Violet vapour, colouring starch paper blue.	<i>Acetic</i> . . .	Smell of vinegar.
<i>Hydrobromic</i> . .	Reddish vapour, colouring starch paper orange.	<i>Hydrofluoric</i> . .	Fuming gas; corrodes glass.
<i>Chloric</i>	Greenish yellow, explosive gas.	<i>Carbonic</i> . . .	Inodorous; gives turbidity with lime-water.
<i>Hypochlorous</i> . .	Yellow vapour; smell of chlorine.	<i>Sulphurous</i> . .	Odour of burning sulphur.
<i>Nitrous, and under certain circumstances nitric acid</i>) vapours.	Brownish yellow, irritating vapours.	<i>Thiosulphuric</i> . .	" and precipitate of yellow sulphur.
		<i>Cyanic</i>	Evolves carbon monoxide, which burns with lavender flame.
		<i>Ferrocyanic</i> . .	" "
		<i>Chromic</i>	Evolves oxygen; solution turns brown or green.
		<i>Oxalic</i>	Evolves carbon monoxide and dioxide without charring; former burns with lavender flame; latter gives turbidity with lime-water.
		<i>Sulphydic</i> . .	Smell of rotten eggs; blackens paper moistened with lead acetate solution.
		<i>Hydrochloric</i> . .	Irritating odour; gives white fumes with ammonia.

* This acid, or arsenious, if present, will have already been discovered among the bases; so also will chromic acid. (See page 121.)

TABLE M.

SYSTEMATIC TESTING FOR INORGANIC ACIDS (INCLUDING OXALIC, FERROCYANIC, FERRICYANIC, AND THIOCYANIC ACIDS.)

If metals other than those of the sixth group have been detected, boil for some time a considerable quantity of the original substance with a *large excess* of sodium carbonate and some water,* filter, and wash the insoluble matter three or four times with hot water. Divide the filtrate into two parts, a smaller and a larger.

A. *Treatment of smaller portion* :—Take successive small portions and test them as follows :

- (1) Acidify with hydrochloric acid and add barium chloride : white precipitate = SULPHURIC ACID or HYDROFLUOSILICIC ACID (distinguish by sulphuric acid test, p. 135).
- (2) Acidify with hydrochloric acid and test for BORIC ACID with turmeric paper (p. 137).
- (3) Add dilute sulphuric acid until just neutral, and then ferric chloride :

Red colour, destroyed by hydrochloric acid = ACETIC ACID.
 „ „ not destroyed by hydrochloric acid = THIOCYANIC ACID.

Dark greenish-blue precipitate = FERROCYANIC ACID. In this case add excess of ferric chloride, filter, and add stannous chloride to the filtrate ; dark greenish-blue precipitate = FERRICYANIC ACID.

- (4) Acidify with dilute sulphuric acid and test for HYDROCYANIC ACID by the ammonium sulphide test (p. 146.)
- (5) Acidify with acetic acid and add calcium chloride ; white precipitate = OXALIC ACID.
- (6) Acidify with dilute sulphuric acid and add ferrous sulphate ; brown colour = NITROUS ACID. *If nitrous acid is absent*, test at once for NITRIC ACID in the same portion of liquid by careful addition of sulphuric acid (p. 149). *If nitrous acid is present*, boil another portion of the solution for ten or fifteen minutes with a considerable quantity of ammonium chloride ; dilute, cool, and then test for nitric acid.†
- (7) Add two or three drops of a solution of oxides of nitrogen in sulphuric acid, and test for HYDRIODIC ACID by means of carbon bisulphide (p. 143).

* H_3AsO_3 , H_3AsO_4 , and H_2CrO_4 , if present, must be removed before adding sodium carbonate, by saturating the solution acidified with hydrochloric acid with sulphuretted hydrogen and filtering. Sodium carbonate is added to the filtrate after boiling for some time to expel sulphuretted hydrogen.

† If HI , H_4FeCy_6 , and H_3FeCy_6 are present, they must be removed before testing for nitrous and nitric acids (see B).

B. Treatment of larger portion :—

(1) Preliminary.

(a) If hydriodic, ferrocyanic, or ferricyanic acid is present, add dilute sulphuric acid till faintly acid, then a good deal of copper sulphate solution, and then a solution of sulphur dioxide till the liquid smells strongly of this oxide, boil (see (d), p. 144, and VII. (d) and VIII. (d), p. 155), and filter.

(b) If hydriodic, ferrocyanic, and ferricyanic acids are absent, proceed at once to (2).

(2) Take successive small portions of the filtrate and test them as follows :—

- (a) Make slightly alkaline by potash, boil, filter, to filtrate add one drop of indigo solution and then acidify with dilute hydrochloric acid; instant decolourisation of indigo = HYPOCHLOROUS ACID; slow decolourisation with evolution of reddish gas = NITROUS ACID; if the indigo is not decolourised add a small quantity of sulphurous acid solution, decolourisation of the indigo = CHLORIC ACID.*
- (b) Add nitric acid, then add solution of ammonium molybdate in nitric acid, and warm gently; yellow precipitate = PHOSPHORIC ACID.†
- (c) Test for HYDROBROMIC ACID by adding chlorine water and carbon bisulphide (p. 143).
- (d) Test for HYDROCHLORIC ACID by adding silver nitrate. If hydrobromic acid is present it must be removed by adding potassium permanganate solution in slight excess, boiling for ten or fifteen minutes and filtering, before testing for hydrochloric acid.

* If hypochlorous acid is present acidify another portion of the liquid with sulphuric acid, boil till all chlorine is expelled, cool, and then add a drop of indigo solution and sulphurous acid.

† Silicic acid, if present, must be removed by evaporating the solution to dryness with slight excess of hydrochloric acid, moistening the residue with strong hydrochloric acid, dissolving in water, and filtering.

TABLE N.

EXAMINATION OF INSOLUBLE SUBSTANCES.

In this Table are included Silicates and Silica; Alumina; Sulphates of Barium, Strontium, and Lead; Chloride, Bromide, and Iodide of Silver; Fluoride of Calcium; Tin, Antimony, and Chromium Oxides; Lead Sulphide, Carbon and Sulphur.

Heat a portion of the substance in a dry tube.

A. It fuses.	B. It is infusible.
<p>(a) <i>Volatile</i>s. SULPHUR. Smell of sulphur dioxide.</p> <p>(b) <i>Does not volatilise</i>. SILVER IODIDE, CHLORIDE, or BROMIDE. (Match test, Table B, C 2.)</p>	<p>(a) <i>After heating, it disappears</i>. CARBON.</p> <p>(b) <i>It is white, unaltered by heating</i>. Lead, barium, or strontium sulphate, calcium fluoride, silica or alumina.</p> <p>1. Match-test for LEAO. (Table B, C₂.)</p> <p>2. Bead of microscopic salt in Bunsen flame for SILICA. (VIII. (b), p. 140.)</p> <p>3. Heat in loop of platinum wire in flame, moisten with cobaltous nitrate, and heat again. Blue mass = ALUMINA.</p> <p>4. CALCIUM FLUORIDE. See p. 138, VI. (c).</p> <p>5. BARIUM OF STRONTIUM SULPHATE fused with sodium carbonate, gives on addition of hydrochloric acid, barium or strontium chloride, former giving green flame coloration, latter crimson.</p> <p>(c) <i>It becomes darkened on heating, but original colour returns on cooling</i>.</p> <p>(d) <i>It is coloured (green), and unaltered by heating</i>.</p> <p>(e) <i>It is black</i>.</p> <p>TIN or ANTIMONY OXIDE. (Match-test, Table B, C₂ and 3.)</p> <p>CHROMIC OXIDE (or chrome iron ore). (Table B, B₂.)</p> <p>LEAD SULPHIDE. (Table B, C₂.)</p>

Further tests may be applied by fusing the substance with 3 to 4 times its weight of a mixture of sodium and potassium carbonates (if any reducible metals, as lead or silver, are present, a porcelain crucible must be used); extract fused mass with water when cold, filter; acidify filtrate with hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, add water, and filter; test any insoluble substance for silica; neutralise the filtrate with Na₂CO₃; and proceed according to Table M.

The portion of the fused mass insoluble in water is dissolved in acid (hydrochloric, if lead and silver are absent), and tested for the bases.

TABLE O.
SEPARATION OF ORGANIC ACIDS.

Dissolve original in water or acid, add large excess of Sodium Carbonate, boil for some time, filter, wash with hot water, add a *very slight* excess of dilute nitric acid to filtrate, boil off all carbon dioxide, exactly neutralise with dilute soda, and add *Calcium Chloride*.*

The precipitate by calcium chloride, after standing 15 or 20 minutes, is filtered off.

A. <i>Precipitate</i> . (Calcium oxalate and tartrate.) Wash <i>well</i> ; add cold caustic potash solution.		C. To another portion of the neutral solution add ferric chloride; filter	
<i>Residue</i> .	<i>Solution</i> .	<i>Precipitate</i> .	<i>Filtrate</i> .
CALCIUM OXALATE. (Confirm by V. (c), p. 138.)	CALCIUM TARTRATE. Reprecipitated on boiling.	Boil with ammonia and filter: to part of filtrate add hy- drochloric acid; white precipitate separating in crys- tals = BENZOIC ACID; to another part add barium chloride, filter if necessary, and then add alcohol; white precipitate = SUC- CINIC ACID.	Has a red colour: boil; reddish pre- cipitate = ACETIC or FORMIC ACID. Distinguish by adding mercuric chloride to the original solution. (See VI. (c), p. 155.)
Boil for some time. CALCIUM CITRATE is precipitated, which is soluble in hydro- chloric acid, but reprecipitated on addi- tion of ammonia and boiling. Filter: add thrice the volume of alcohol, and filter.		<i>Precipitate</i> .	<i>Filtrate</i> .
SUCCINIC ACID. Neutralise with hy- drochloric acid, and add ferric chloride. Buff-coloured pre- cipitate.—BENZOIC ACID. (III. (b), p. 153.)		<i>Precipitate</i> .	<i>Filtrate</i> .

Another portion of the original solution is distilled with sulphuric acid, distillate neutralised with sodium carbonate, and evaporated to dryness. One part is tested for ACETIC ACID by V. (b), (d), p. 154; the other part is dissolved in water, and tested for FORMIC ACID by VI. (b), p. 154.

TANNIC and GALLIC ACIDS must be separately tested for in the original solution. With the first of these gelatin produces a *yellowish flocculent precipitate*; with the latter *no precipitate*. Ferric chloride in both solutions produces a bluish-black precipitate.

* If sodium carbonate gives no precipitate this treatment may be omitted, and the calcium chloride added to a neutral liquid, obtained by dissolving original in water, or in acid and neutralising by dilute soda.

E. REACTIONS OF SOME ORGANIC COMPOUNDS.

I. ETHYL ALCOHOL, $C_2H_5(OH)$:—

(a) A colourless liquid ; miscible in all proportions with water ; completely volatile on the water-bath.

(b) Shake the cold liquid with a few drops of benzoyl chloride, allow the oily liquid to settle, remove it by means of a pipette, and then warm it with a drop or two of caustic soda solution ; the soda dissolves the excess of benzoyl chloride, and the characteristic aromatic odour of ethyl benzoate is then perceived.

(c) Add a few drops of caustic soda solution, warm to about 50° , add a saturated solution of iodine in potassium iodide drop by drop until the liquid acquires a yellowish-brown colour, then add soda very carefully until the solution is just decolourised. If alcohol is present, a yellow precipitate of *iodoform* (CHI_3) is gradually deposited. Under the microscope this precipitate is seen to consist of hexagonal plates, frequently arranged in stellate groups. Many other organic bodies—*e.g.*, aldehyde, propyl alcohol, sugar—give the same reaction. It is not, however, given by chloroform, methyl alcohol, glycerol, or ether.

(d) 50 c.c. of the liquid are mixed with 1 c.c. of a saturated solution of potassium dichromate and 6 c.c. of dilute sulphuric acid (1 in 20), and about 20 c.c. of the mixture distilled over into a tube containing about 20 c.c. of a very strong solution of caustic soda, a few fragments of clean pumice being placed in the retort to prevent bumping. The distillate is then boiled for a short time and set aside for an hour or two ; if the original liquid contained alcohol, the distillate will now have a yellow colour, and if more than one-tenth of a per cent. of alcohol was present, it will have deposited brownish-yellow aldehyde resin.

If the solution to be tested contains only very small quantities of alcohol, a quantity of it should be distilled, and the above tests applied to the first portion of the distillate.

II. METHYL ALCOHOL, $\text{CH}_3(\text{OH})$ —(Wood spirit):—

(a) A colourless mobile liquid ; miscible in all proportions with water ; more volatile than ethyl alcohol.

(b) With free iodine, methyl alcohol gives no precipitate of iodoform. (Compare I. (c), p. 171.)

(c) When treated with oxidising agents, methyl alcohol yields formic acid. About 5 c.c. of the liquid is mixed with 15 c.c. of water, 5 c.c. of conc. sulphuric acid and 2 grams of potassium dichromate added, the mixture allowed to stand for about 15 minutes, and about 12 c.c. then distilled over. The distillate is neutralised with sodium carbonate, concentrated by evaporation, slightly acidified with acetic acid, and tested for formic acid with silver nitrate or mercuric chloride (p. 154). Ethyl alcohol when treated in a similar manner yields only very minute quantities of formic acid.

III. GLYCEROL, $\text{C}_3\text{H}_5(\text{OH})_3$:—

(a) A colourless viscid liquid with a very sweet taste ; miscible in all proportions with water and with alcohol ; insoluble in pure chloroform and in benzene ; practically non-volatile on the water-bath.

(b) Two drops of glycerol are carefully heated with two drops of fused phenol and the same quantity of conc. sulphuric acid in a dry test-tube to a little above 120° , until a solid mass forms in the fused mixture. After cooling, water is added, together with a few drops of ammonia ; the *glycereïn* ($\text{C}_9\text{H}_{10}\text{O}_2$) which has been formed then dissolves, with production of a beautiful carmine-coloured solution.

(c) Powdered borax is moistened with the glycerol solution, and introduced into a Bunsen flame on a platinum wire ; the glycerol liberates boric acid, which imparts to the flame its characteristic green colour. If the solution is dilute it must be concentrated by evaporation on the water-bath before applying this test.

If, as frequently happens, the glycerol is mixed with

sugars or other organic substances, these must be removed before applying the above tests. The liquid is mixed with a greater or less quantity of finely powdered quicklime according to the amount of sugar present, an equal bulk of fine sand added, and the mixture evaporated on the water-bath to a pasty consistency. After cooling, the hard mass is powdered, and treated in a closed flask with 80 to 100 c.c. of a mixture of equal volumes of absolute alcohol and ether, the liquid filtered, and evaporated on the water-bath, when the glycerol is left as a viscid liquid, to which the above tests may be applied. In applying test (*b*) the fused substance, after cooling, should first be treated with pure water in order to remove the carbonaceous products formed by the action of the heat on the small quantity of admixed organic substances, and then treated with water and ammonia to dissolve the glycerein.

IV. PHENOL (CARBOLIC ACID), $C_6H_5(OH)$:—

(*a*) Pure phenol is a white crystalline solid which melts at 42° , and is only sparingly soluble in water, but dissolves readily in alcohol and in ether. Phenol and many of its metallic derivatives (carbolates or phenolates) have a characteristic smell.

(*b*) Ferric chloride produces an intense violet colouration. The colour is discharged by dilute acids, and the reaction is prevented by many inorganic salts and organic compounds, as for example, sodium and ammonium acetates, borax, disodium-hydrogen phosphate, glycerol (compare V. (*a*), p. 174), alcohol, and ether.

(*c*) Bromine water produces a white precipitate of tribromophenol, $C_6H_2Br_3(OH)$, which forms slowly in dilute solutions and is distinctly crystalline. When warmed with water and a small quantity of sodium amalgam, the tribromophenol is reduced to phenol, and on acidifying with sulphuric acid the phenol can be recognised by its smell.

(*d*) The solution is mixed with ammonia and warmed

with a small quantity of sodium hypochlorite (not in excess); a deep blue colouration is produced, turned red by acids.

(e) The solution is mixed with a small quantity of mercurous nitrate solution and boiled; a deep red colouration is produced.*

V. SALICYLIC ACID, $C_6H_4(OH)CO.OH$:—

(a) Ferric chloride produces an intense purple colouration. This reaction is far more delicate than the corresponding reaction with phenol, and is not appreciably affected by the presence of considerable quantities of glycerol (compare IV. (b), p. 173). It is interfered with by dilute mineral acids, by alkalies, and by certain other substances, *e.g.*, sodium and ammonium acetates, tartaric, citric, and oxalic acids, borax, and disodium-hydrogen-phosphate.

(b) Silver nitrate produces a white precipitate in neutral solutions, but not with the free acid.

(c) Bromine water throws down a white precipitate, which, when treated with sodium amalgam, yields phenol. (Compare IV. (c), p. 173.)

VI. DEXTROSE, GLUCOSE, or GRAPE SUGAR, $C_6H_{12}O_6$:—

(a) Dextrose is not blackened by conc. sulphuric acid in the cold, but unites with it, forming a yellowish compound.

(b) The solution is mixed with two drops of copper sulphate solution, made alkaline by addition of a small quantity of caustic soda solution, and heated; the copper sulphate is reduced and red cuprous oxide is precipitated.

(c) The solution is mixed with a small quantity of Fehling's solution, and heated; red cuprous oxide is precipitated.

* If the mercurous nitrate is perfectly free from nitrous acid, which rarely happens, this reaction will not take place.

VII. SACCHAROSE OR CANE SUGAR, $C_{12}H_{22}O_{11}$:—

(a) The solid substance, or a conc. solution, is carbonised by conc. sulphuric acid in the cold.

(b) A freshly prepared solution of cane sugar does not reduce Fehling's solution (compare VI. (c), p. 174), but if boiled for some time with dilute sulphuric acid, the cane sugar is converted into a mixture of dextrose and levulose, which readily reduces the Fehling's solution.

(c) A solution of cane sugar does not reduce an alkaline solution of copper sulphate, unless the sugar has previously been boiled with dilute acid (compare VI. (b), p. 174).

VIII. STARCH $(C_6H_{10}O_5)_x$:—

(a) Under the microscope starch is seen to have a characteristic organised structure, the shape and average size of the granules varying with the nature of the plant from which the starch has been derived.

(b) Free iodine produces an intense blue colouration even with very small quantities of starch. To apply this test, the liquid is mixed with a small quantity of potassium iodide solution, and dilute chlorine water added drop by drop until the blue colour appears ; or better, after addition of potassium iodide, two drops of potassium dichromate solution are added, and then dilute hydrochloric acid very carefully drop by drop with agitation. In very dilute solutions the colouration is deep green. On heating the liquid the blue colour is entirely discharged, but reappears on cooling.

SECTION III.

DETECTION OF THE RARE ELEMENTS.

HITHERTO we have confined our attention to those elements or combinations of elements which are of common occurrence. There are, however, many of the so-called 'rare elements,' which are found very widely scattered among the mineral constituents of the earth; but, as they generally exist in only small quantities in any one mineral, there is occasionally some difficulty in detecting them.

DIVISION I.

Metals belonging to Group I. precipitated on addition of Hydrochloric Acid, **Thallium, Tungsten, and Niobium.**

1. **THALLIUM.**—The commonest source of thallium is *iron pyrites*.

One part of thallium in 10,000 parts of this mineral may be detected by the following process:—

After solution of the finely-powdered mineral in aqua regia, sulphuric acid is added, and the solution is evaporated until the nitric acid is driven off. On addition of sodium sulphite, the iron and thallium are reduced to protosalts; from this solution potassium iodide precipitates, after a little time, bright-yellow thallium iodide.

The black residue which remains when zinc is dissolved in sulphuric acid often contains thallium; this is dissolved in nitric acid, the solution evaporated with sulphuric acid, &c., and treated as above described. In the spectroscope thallium salts yield a characteristic green line, see Chart of Spectra.

II. **TUNGSTEN, W: AND NIOBIUM, Nb.**—Tungsten is generally found associated with iron and manganese, and

sometimes with niobium in the mineral *wolfram*. To detect tungsten, the finely-powdered mineral is digested with strong hydrochloric acid, finally with addition of a little nitric acid. Iron and manganese are thus dissolved; the residual tungstic acid is dissolved in ammonia (if any white insoluble matter remains, remove it by filtration, *vide infra*), the solution is evaporated to dryness, and the residue ignited; pale-yellow tungstic oxide (WO_3) then remains. Heat a small portion of this with microcosmic salt in the reducing flame; a pure blue-coloured bead is obtained. The white portion, insoluble in ammonia, contains the niobic acid; it is tested in the microcosmic bead; in the oxidising flame it gives a colourless bead, and in the reducing flame a bluish-violet bead. On adding a trace of ferrous sulphate, the colour changes to blood-red.

Before testing for niobium, every trace of tungstic oxide must be removed, as it gives reactions very similar to those afforded by niobium oxide.

DIVISION II.

Metals belonging to Group II.

Palladium, Rhodium, Osmium, Ruthenium. (Div. I.,
Platinum, Iridium, Gold, Molybdenum, Selenion, Tellurium. (Div. II.)

PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM, PLATINUM, AND IRIDIUM.—These metals are generally found associated together in the so-called *platinum ores*. Iridium is often present in certain ores of gold. By heating nearly to boiling, a quantity of the platinum ore, with five parts fuming hydrochloric and one part fuming nitric acid, in a small retort to which a well-cooled receiver is adapted, a distillate is obtained in which osmium (existing as osmic

tetroxide, OsO_4) may be detected by adding potassium nitrite ; potassium osmite, a red salt, being formed ; or by adding sodium sulphite, when the solution turns violet, and after a time deposits blue osmium sulphite (OsSO_3).

The solution in the retort is separated from any black insoluble matter (consisting of osm-iridium), evaporated to dryness, the residue again evaporated with a little hydrochloric acid, and finally dissolved in water. On adding a few drops of this solution to a solution of sodium thiosulphate containing a little ammonia in a test-tube, a pale lemon-colour changing to brown, and eventually—on boiling—to black, is produced, if palladium is present.

To another portion of the solution concentrated by evaporation ammonium chloride is added ; platinum and iridium are thus precipitated as double chlorides. Wash with cold water, and in the filtrate precipitate palladium (as PdCy_2), by addition of mercuric cyanide ; after removing this precipitate, sodium carbonate is added in excess, then hydrochloric acid, the solution evaporated to dryness, and the residue treated with alcohol. Any insoluble matter consists of sodium chlororhodate.

Any ruthenium present in the solution may be detected, after the removal of the palladium, by boiling with a little hydrochloric acid, and adding ammonia to alkaline reaction. On now adding a solution of sodium thiosulphate and boiling, a fine red-purple colour (black by transmitted light) is produced in the liquid.

GOLD may be detected when existing in minute quantities by the following process : five or ten grams of the finely powdered mineral are shaken with alcoholic tincture of iodine, the insoluble matter is allowed to settle, a piece of Swedish filter paper is dipped into the solution, and incinerated after drying. If the ash be purple in colour, gold is present. To confirm the presence of gold, treat the ash with a few drops of aqua regia, evaporate to dryness at a gentle heat, and dissolve the residue in water ; pour this solution into a beaker

which is set upon a sheet of white paper. A solution is now prepared by adding ferrie ehloride to stannous ehloride until a permanent yellow colour is produced. This solution is diluted, a glass rod is dipped into it, then into the gold solution ; a bluish-purple streak in the track of the rod confirms the presenee of gold.

SELENION is sometimes found in specimens of native sulphur. Its presence may be detected by heating the powdered substance in potassium eyanide solution on the water bath for some hours (metals forming soluble compounds with potassium eyanide are assumed to be absent). On the addition of hydroehloric acid to this solution selenion only is precipitated. This preeipitate, exposed on the prepared match to the reducing Bunsen flame, evolves an odour of decaying horse-radish.

The deposit which forms in the sulphurie acid chambers sometimes contains selenion. It is dried, deflagrated with potassium nitrate and earbonate in a red-hot erucible, the residue, which contains potassium selenate, is digested with hydroehloric acid, evaporated to a small bulk, saturated with sulphur dioxide, and boiled. Red flakes of selenion are preeipitated.

MOLYBDENUM occurs in *molybdenite* as sulphide, and in *wolframite*, combined with lead. The mineral is treated with dilute hydroehloric acid until any iron and zinc present are dissolved, the acid is poured off, and the residue treated with cone. hydroehloric acid, and finally evaporated to dryness. The mass is digested with ammonia, filtered, and the ammoniacal solution evaporated down. On cooling, crystals of ammonium molybdate are deposited, which may be dissolved in nitric acid. This solution, on addition of sodium phosphate, gives a yellow precipitate.

TELLURIUM occurs native, associated with bismuth, lead, gold, and silver ; sometimes also with selenion.

The mineral, in fine powder, is fused, with ten times its weight of potassium eyanide, in a long-necked flask through

which a stream of hydrogen is passed. Potassium telluride is formed. The residue is dissolved in water, and a current of air passed through the solution, whereby the tellurium is precipitated in metallic scales.

These scales, heated on the charcoal splinter, are volatilised, forming a white deposit of tellurous oxide on the charcoal. A slightly acid smell is alone produced, very different from the strong odour produced by selenion compounds (*vide supra*).

DIVISION III.

Metals belonging to Group III.

Zirconium, Cerium, Lanthanum, Didymium, Titanium.

ZIRCONIUM usually occurs in nature in *zircons* or *jargons*. These are decomposed by fusing with about five times their weight of pure sodium carbonate, and adding a small piece of pure sodium hydrate after fusion is nearly complete. On treating the fused mass with cold water the silica is removed. The insoluble portion is dissolved in hydrochloric acid, evaporated to dryness, and the residue treated with water acidulated with hydrochloric acid; the solution now contains nearly pure zirconium chloride. From this solution oxalic acid throws down a bulky precipitate of zirconium oxalate, soluble in hydrochloric acid.

Ammonium carbonate precipitates zirconium carbonate, soluble in excess of the precipitant, but reprecipitated on boiling. Potassium sulphate added to a hot solution of zirconium salts precipitates zirconium sulphate, insoluble in water, and in hydrochloric acid, if precipitated in cold solutions; if precipitated in hot solutions, the precipitate is soluble in a large excess of hydrochloric acid.

CERIUM, LANTHANUM, and DIDYMIUM, occur together in

the mineral *cerite*. The powdered mineral is boiled for an hour with hydrochloric acid ; from the filtered solution, excess of ammonia precipitates everything but the lime. This precipitate is redissolved in nitric acid, the solution diluted with water, a small quantity of peroxide of lead added, and the liquid boiled ; the cerium is indicated by the yellow colour produced in the liquid. Potash produces a white precipitate in this liquid insoluble in excess, but gradually becoming yellow on standing. This liquid is evaporated to dryness, heated to expel a portion of the acid, and the residue treated with boiling water, acidulated with nitric acid ; lanthanum and didymium are alone dissolved. The residue gives a yellow-red borax bead in the oxidising flame. By evaporating this solution, the lead having been removed by sulphuretted hydrogen, precipitating with ammonium oxalate, igniting, dissolving the oxides in nitric acid, evaporating to dryness, heating the residue to 400° , and subsequently adding hot water and filtering, lanthanum nitrate is dissolved ; in this solution potash throws down lanthanum hydrate, which yields a colourless borax bead. The portion insoluble in hot water consists of didymium subnitrate ; with microcosmic salt in the reducing flame an amethyst bead is obtained ; with sodium carbonate in oxidising flame a white mass is formed.

TITANIUM generally exists as oxide TiO_2 in certain iron ores, in many silicates, and in some iron slags. To detect it fuse the powdered substance with eight times its weight of potassium bisulphate, triturate the mass with cold water until all is dissolved excepting silica, filter, add sodium thio-sulphate to the filtrate, and boil ; a yellowish-white precipitate (TiO_2) shows the presence of titanium ; with microcosmic salt in the oxidising flame, it gives a colourless glass ; in the reducing flame the bead is yellow while hot, red while cooling, and violet when cold. With a trace of ferrous sulphate, a blood-red bead is obtained in the reducing flame.

DIVISION IV.

Metals belonging to Group IV.

Uranium and Indium.

URANIUM occurs in a few minerals, most abundantly in *pitchblende* and *uranite*. To detect its presence in these substances, where it is usually mixed with iron, &c., advantage is taken of the fact that its carbonate is soluble in excess of ammonium or sodium carbonate, in which respect it differs from iron. To prove the presence of uranium, dissolve a portion of the mineral by boiling with a small quantity of nitric acid, dilute with water, add a tolerably large excess of a solution of sodium carbonate, and boil; filter from insoluble carbonates of iron, calcium, &c., and to the filtrate add caustic potash; a yellow precipitate of uranic oxide (UO_3) is formed. In the borax bead a yellow glass, becoming yellow-green on cooling, is produced by heating in the oxidising flame; in the reducing flame the bead is green both when hot and cold.

INDIUM is found in some specimens of *zinc blende*. The sample is almost entirely dissolved in hydrochloric acid. After about twenty-four hours the clear liquid is poured off, the residue is treated with a few drops of sulphuric acid, washed with hot water until it has no longer an acid reaction, nitric acid is added, and a few drops of sulphuric acid, the liquid evaporated nearly to dryness, water added, and the solution separated by filtration. Ammonia in large excess is added to the filtrate, the ensuing precipitate collected, well washed, dissolved in a few drops of hydrochloric acid, acid sodium sulphite added in excess, and the solution boiled. A basic salt, having the composition $2\text{In}_2\text{O}_3 \cdot 3\text{SO}_2 \cdot 8\text{H}_2\text{O}$, separates out. On the charcoal splinter white ductile metallic beads are obtained. On the asbestos thread a violet-blue colouration is imparted to the flame.

DIVISIONS V. and VI.

Vanadium, Lithium, Cæsium, Rubidium.

VANADIUM occurs in many lead ores, also in small quantities in several other minerals, and in certain sandstone beds containing copper. To detect vanadium decompose the mineral with conc. nitric acid, add sulphuric acid, and filter from insoluble lead sulphate (wash this precipitate with alcohol); the filtrate contains vanadium pentoxide (V_2O_5). On addition of zinc, the solution goes through a series of changes in colour, ultimately a violet solution being obtained, which, on standing in the air, turns brown by oxidation, or if excess of acid be present becomes green.

The three alkaline metals, LITHIUM, CÆSIUM, and RUBIDIUM, occur in the mineral *lepidolite* and in certain mineral waters. They seem to be very widely diffused, occurring, however, generally in but minute quantities. To detect them in *lepidolite*, fuse the powdered mineral, pour it into cold water, pulverise and wash, then add about twice its weight of hydrochloric acid, and boil for some time; filter, add a little nitric acid, and boil to peroxidise iron; *dilute the solution* and add sodium carbonate, filter and boil down the filtrate; now add hydrochloric acid in excess, and platinum tetrachloride; cæsium, and rubidium are thus precipitated as double chlorides Cs_2PtCl_6 and Rb_2PtCl_6 . In the filtrate, after removing excess of platinum by means of sulphuretted hydrogen, and concentration of the liquid, sodium carbonate precipitates lithium carbonate (confirm by testing in Bunsen flame or spectroscope).

To detect lithium in mineral waters evaporate part of the water to a small bulk, add baryta water, and, on cooling, ammonium carbonate, and filter; add sodium phosphate to the filtrate, evaporate to dryness, and treat the residue with a very small quantity of water. Lithium phosphate remains behind, and may be tested in the spectroscope.

To detect these 'rare metals' in the ordinary course of analysis the following method may be pursued:—

The precipitate of Group I. is boiled in water. Lead and thallium chlorides are thus dissolved; filter, and to the filtrate add dilute sulphuric acid. To the filtrate from the precipitated lead sulphate add potassium iodide; a yellow precipitate (TII) indicates thallium (confirm by the spectroscope). That portion of the group precipitate which is insoluble in boiling water is treated with ammonia to remove the silver chloride from the residue. The mercury is removed by treatment with nitric acid. The insoluble part is now tested in the borax bead for tungsten (see p. 177).

That portion of the precipitate by sulphuretted hydrogen which is insoluble in ammonium sulphide may contain the sulphides of the rare metals, palladium, rhodium, osmium, and ruthenium.

The precipitate is to be fused with caustic potash and potassium chlorate, the fused mass treated with water, and filtered. Ruthenium is tested for in a portion of the filtrate by boiling with a little dilute hydrochloric acid, adding ammonia in slight excess, and then boiling with sodium thiosulphate solution; a purple-red colour indicates ruthenium. Another portion of the filtrate is distilled after addition of nitric acid, and osmium tested for in the distillate according to test on p. 178.

That part of the fused mass which was insoluble in water is to be dried, gently ignited in a stream of hydrogen, the reduced metals very gently heated with dilute nitric acid, whereby copper, lead, bismuth, and cadmium are dissolved, and the insoluble portion treated with aqua regia. The residue contains any rhodium which may be present. Palladium may be detected in the aqua regia solution by the reaction with sodium thiosulphate (see p. 178). Mercury must be tested for in another portion of the original precipitate by sulphuretted hydrogen.

The precipitate resulting from the addition of acid to the

ammonium sulphide solution (containing the members of Division II.) may contain the sulphides of platinum, iridium, gold, molybdenum, selenion, and tellurium (in addition to those of arsenic, antimony, and tin).

The precipitate is dried, mixed with one part dry sodium carbonate and one part sodium nitrate, and the mixture projected into a porcelain crucible containing two parts sodium nitrate in a state of fusion. The fused mass, when cold, is triturated with cold water, and the aqueous solution separated by filtration. The filtrate contains (in addition to arsenic) the tellurium, selenion, and molybdenum, while antimony, tin, gold, platinum, and iridium remain in the insoluble part.

I. A portion of the aqueous solution is tested for arsenic according to V. (*c*) and (*d*), p. 114.

To another portion, acidified with hydrochloric acid, potassium sulphocyanide is added, and a rod of pure zinc immersed in the liquid; if molybdenum be present, the solution becomes crimson, owing to formation of molybdenum sulphocyanide. The remaining portion of the solution is evaporated to dryness, and the residue fused with potassium cyanide in a stream of hydrogen. The fused mass is then dissolved in water, and a current of air passed through this solution. The whole of the tellurium is thus precipitated in the metallic state.

On adding hydrochloric acid and stannous chloride to the filtered solution a red precipitate of selenion is produced, if that element is present.

II. That portion of the fused mass which is insoluble in water is now to be tested for antimony, tin, gold, platinum, and iridium. Heat it very gently with a saturated solution of tartaric acid, filter, and test the filtrate with sulphuretted hydrogen for antimony. Transfer the residue to a platinum capsule, heat with hydrochloric acid, and add a small piece of pure zinc. If tin be present it is reduced to the metallic state. Cautiously pour off the liquid, wash the residue

thoroughly, and again boil with conc. hydrochloric acid. Test the solution thus obtained for tin (a greyish white precipitate with mercuric chloride), remove the part insoluble in hydrochloric acid to a porcelain dish, and dissolve in aqua regia.

Test one portion of this solution for gold by making use of the reaction with stannous and stannic chlorides (p. 179).

If platinum is present another portion will give, on addition of potassium chloride, a yellow crystalline precipitate of double potassium-platinum chloride (2KCl.PtCl_4), while a third portion, treated with caustic potash, turns deeper red in colour, and eventually, after exposure to the air, becomes azure blue, if iridium is present.

The group precipitate obtained by adding ammonium chloride and ammonia, may contain zirconium, titanium, cerium, lanthanum, and didymium.

The precipitate is dried, ignited, and fused for some time in a platinum crucible with potassium-hydrogen sulphate. On boiling the fused mass with water iron remains in the insoluble portion; the presence of this element may be recognised by dissolving in hydrochloric acid, and applying the tests for iron. The aqueous solution is diluted and boiled for some time, carbon dioxide being led through the liquid; if a precipitate forms filter it off, and test it for titanium in the borax bead (p. 181). To the filtrate add a conc. caustic potash solution, filter and boil the liquid, test any precipitate which forms for chromium, and the filtrate therefrom test for aluminium. Dissolve the precipitate formed by caustic potash in hydrochloric acid, and remove the excess of acid by evaporation (if the precipitate was reddish in colour add barium carbonate and allow to stand for several hours; iron is thus removed; filter, and to the filtrate add sulphuric acid to remove excess of barium, neutralise exactly with potash, and proceed as follows):—add a few crystals of potassium sulphate, boil, and allow the fluid to stand for some hours; now filter and wash with a dilute potassium

sulphate solution, remove the precipitate to a test tube, and boil repeatedly with water and a little hydrochloric acid, the oxides of cerium, lanthanum and didymium are thus dissolved, while the potassium-zirconium sulphate remains undissolved.

The cerium, lanthanum and didymium may be separated by the process given on pp. 180, 181.

Before treating the precipitate of Group IV. with dilute hydrochloric acid, warm it very gently with a conc. ammonium carbonate solution, filter, and test the filtrate for uranium according to the method given on p. 182.

The filtrate from Group IV. may contain vanadium and also traces of tungsten, unprecipitated by hydrochloric acid. To detect these, acidify the liquid with hydrochloric acid, filter and fuse the sulphides with sodium carbonate and potassium nitrate, dissolve the fused mass in water (any residue may consist of nickel oxide), and in one portion of the solution test for vanadium by adding solid ammonium chloride, a white precipitate of ammonium vanadate is obtained if vanadium is present: to the rest of the solution add hydrochloric acid and a piece of zinc, if the liquid becomes blue tungsten is present.*

SECTION IV.

DETECTION OF POISONS.

A. *INORGANIC POISONS.*

(Phosphorus, Arsenic, Antimony, Mercury, Lead, Copper, and Zinc.)

THE general method to be employed when all poisons, inorganic and organic, are to be sought for, is as follows:—

Acidulate the mass, distil, and test the distillate for hydrocyanic acid (XV. (c.), p. 146).

* For further details concerning the rare metals a larger manual must be consulted.

Test the residue for phosphorus by method A or B (*infra*). The residue is tested for alkaloids (see p. 207). All the residues, extracts, &c., are then united, alcohol and ether removed by evaporation, and the mass examined for the metallic poisons (see p. 189).

I. PHOSPHORUS.—First, note whether the substance under examination, when thoroughly stirred up, smells of phosphorus, or is luminous in the dark. A slip of paper moistened with silver nitrate is suspended in the neck of a flask containing a little of the suspected matter, the flask being heated to 30° or 40° . If the paper is not blackened after some time, no unoxidised phosphorus is present, and, consequently, any further examination may be dispensed with. If, however, the paper is turned black, it is absolutely necessary to apply further tests before deciding that phosphorus is actually present.

The following processes may be employed:—

A. The suspected matter, mixed with water and a little sulphuric acid, is boiled in the dark in a flask connected with a Liebig's condenser. If phosphorus is present—even in quantities so small as 1 part in 100,000—a luminous ring appears in the upper part of the inner tube of the condenser. Certain substances—such as alcohol, ether, oil of turpentine, &c.—prevent the luminosity of phosphorus, so that, when such bodies are present, this method fails. Easily volatilised compounds—as alcohol and ether—soon, however, distil over, and the luminosity then appears.

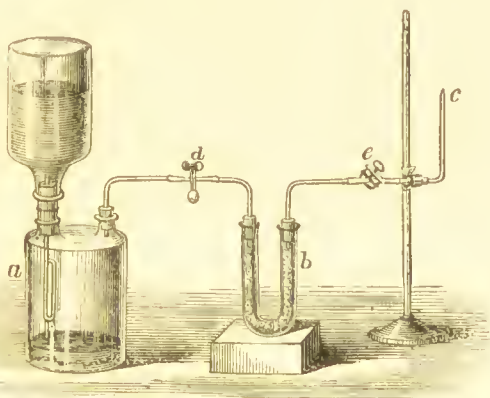
Small globules of phosphorus are found at the bottom of the receiver. These may be collected, dried, and their luminosity in the dark observed.

B. The suspected matter, along with water and dilute sulphuric acid, is warmed gently for several hours in a flask through which a slow stream of washed carbon dioxide is passed, and with which is connected a U-tube, containing silver nitrate solution. If a black precipitate (silver phos-

phide) forms in this solution, it is to be collected and examined as follows, making use of the apparatus shown in fig. 52 :—

a is a hydrogen generator ; *b* contains pumice-stone, moistened with conc. caustic potash ; *c* is a *platinum* jet (kept cool by means of moistened wool) ; *d* and *e* are clips. Hydrogen is generated in *a*, the current of the gas being so regulated that a small, steadily-burning flame is obtained at *c* ; if this flame shows no green inner cone, and

FIG 52.



no emerald colouration when caused to impinge upon porcelain, we may conclude that the gas is free from phosphoretted hydrogen. The precipitate is now to be washed into *a* (through the upper flask), and the flame at *c* noticed. If even a trace of silver phosphide existed in the precipitate, a green cone becomes visible in the centre of the flame, which also shows an emerald colouration when it impinges on porcelain. This method is applicable in the presence of substances which hinder the reaction of method A.

II. METALLIC POISONS.—*Arsenic, Antimony, Mercury, Lead, Copper and Zinc.*—The viscera to be examined are

placed in a large porcelain dish, there turned inside out, and carefully examined for small white grains of arsenious oxide.

As this substance is but slightly soluble in water, part of it not unfrequently remains in the undissolved state imbedded in the coats of the stomach, &c. If any such particles are found, they must be carefully dried by pressing between folds of blotting paper, and reserved for examination. After mixing all the contents of the dish together, one-third is set aside, and the remaining two-thirds mixed with distilled water, thoroughly stirring up the mass with a glass rod.

After standing a few minutes, pour the fluid into another dish; repeat this operation several times, and finally carefully feel the residue in the dish with a glass rod to make sure that no small gritty particles remain in it. If any such are found, remove them, dry them, and reserve them for examination (see p. 200).

If time or the condition of the substance to be examined permit, the semi-liquid mass may now be submitted to dialysis. The dialyser consists of a round sheet of parchment paper, 30–35cm. diam., spread over a gutta percha hoop, 5cm. deep and 20–25cm. diam. The paper being previously wetted, another hoop is slipped over the first, so as to secure the paper. When the upper surface of the paper is wetted with a sponge, no drops should show themselves on the under surface. The liquid, after twenty-four hours' digestion at 32° , is poured into this dialyser, covering the paper to the depth of 12mm. or so, and the whole is floated on water in another dish (see fig. 53). After twenty-four hours the greater portion of the dissolved arsenious oxide or other metal will have passed into the outer water. The dialysate is to be concentrated by evaporation on the water-bath, acidulated with hydrochloric acid, and treated with sulphuretted hydrogen, as directed on p. 185. The principal advantage of this method is that the poisons are obtained in a pure state in the dialysate, separated from

colloidal organic matter. If no poison be detected, test the residue on the dialyser as directed in the following section :—

Care must of course be taken to insure the purity of the reagents used in all these operations.

The semi-liquid mass on the dialyser, or, if dialysis has not been resorted to, the original substance, is heated on the water-bath. A quantity of pure hydrochloric acid (Sp. Gr. 1.12), about equal in weight to the amount of solid substance, is added, together with distilled water, if necessary, sufficient to form a thin paste. Continue to heat the mixture on the water-bath, and add potassium chlorate, in quantities of about two grammes at a time, until a light yellow homogeneous fluid is obtained. The water lost by evaporation is to be replaced from time to time.

FIG. 53.



After a further addition of potassium chlorate, and when the liquid is cool, filter it, wash the residue well with hot water, collecting the washings separately from the filtrate. The filtrate is heated on the water-bath until it no longer smells of chlorine (evaporated water being replaced). The washings are evaporated to about 100 cc., and added to the filtrate. The liquid is now transferred to a flask, heated to about 70° , and a slow current of washed sulphuretted hydrogen passed through it for about twelve hours; after which the flask is covered over, and allowed to stand in a moderately warm place for twelve hours or so; if the liquid now no longer smells of sulphuretted hydrogen, it must be again treated with the gas. Collect the precipitate which

may have formed on a filter, and wash it (at first with water containing sulphuretted hydrogen) until the washings are free from chlorine. If no precipitate has been produced by the sulphuretted hydrogen, the liquid should be concentrated by evaporation at a gentle heat, and the gas again passed through it.

The precipitate may contain the sulphides of arsenic, antimony, mercury, copper, or lead, in addition to a considerable quantity of organic matter.

The filtrate, which may contain zinc, is concentrated by evaporation, transferred to a flask, ammonia and ammonium sulphide added, the flask corked up, and set aside for further examination (see p. 202). The precipitate is now to be dried in a small dish on the water-bath; pure fuming nitric acid (which must be free from chlorine) is then added, so as to completely moisten the mass, which is then evaporated to dryness on the water-bath. The residue is moistened with pure conc. sulphuric acid, and heated first on the water, then in the air-bath, at about 170° , until the mass is friable. If this state is not at once obtained, a few cuttings of Swedish filter paper are added, and the heating continued. Now warm the residue with 1 part of hydrochloric acid and 8 parts water; filter, wash with hot water, and reserve the residue for examination (Residue A).

The filtrate must now be again saturated with sulphuretted hydrogen gas, attending to the directions already given, and the ensuing precipitate collected and washed. This precipitate is now perfectly free from organic matter.

Note the colour of the Precipitate.

If it is light yellow, probably arsenic only is present. Shake up a small portion with ammonia in a test-tube; if it dissolves entirely (*infra*) arsenic is the only metal present. If, however, it does not entirely dissolve, or if the precipitate is not yellow, you must test for other metals besides arsenic.

If arsenic is the only metal present, treat the precipitate on the filter with ammonia, whereby everything is dissolved (except perhaps a little sulphur). Evaporate the ammoniacal solution to dryness on the water-bath, and reserve it for subsequent examination. (B. *infra*.)

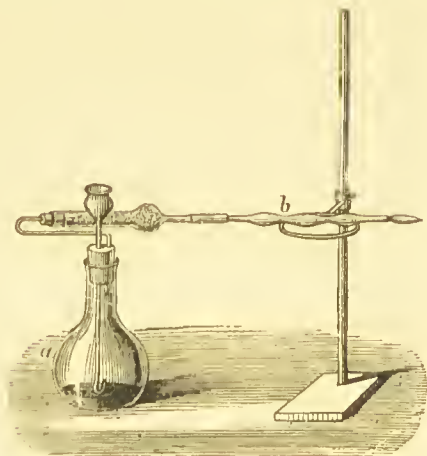
If other metals than arsenic are present, spread out the filter with the precipitate in a porcelain dish; add a little ammonia and ammonium sulphide, and then wash the solid matter off the filter with the smallest possible quantity of water; remove the filter, and gently heat the residue in the basin. Filter, wash, and reserve the residue for examination (Residue C., p. 201). The filtrate and washings are now evaporated to dryness, pure fuming nitric acid added, and the mass gently heated; when dry, add a little caustic soda, which neutralises the acid without effervescence; add now a mixture of 1 part carbonate and 2 parts nitrate of sodium, free from chlorine; evaporate to dryness, and heat gradually until the mixture fuses to a colourless liquid. When cold treat the mass with cold water, and filter. Arsenic thus goes into solution as sodium arsenate, while antimony remains on the filter as sodium antimonate; filter; set aside the insoluble portion (D. see p. 202); add pure dilute sulphuric acid to the filtrate, and evaporate in a porcelain dish, adding a little more sulphuric acid towards the end of the operation. If arsenic was the only metal present, the residue B (*vide ante*) is treated with fuming nitric acid, and the resultant liquid evaporated down with sulphuric acid until all nitric or nitrous acid is expelled. Two methods may be employed for the further examination of this liquid.

1. *Marsh's Process*.—This method is based upon the fact that arseniuretted hydrogen (AsH_3) is formed when nascent hydrogen acts on a soluble arsenical compound, and that this gas, arseniuretted hydrogen, is readily decomposed by heat, yielding metallic arsenic.

A very convenient and easily-constructed form of apparatus is shown in fig. 54. It consists of a small, wide-

mouthed flask, *a*, capable of holding about 300 cc., fitted with a good caoutchouc cork,* which is perforated with two holes; through one of these passes a funnel tube, and through the other a glass tube, bent at right angles, and passing through a small cork into a small bulb-tube containing lumps of perfectly dry calcium chloride. To the other end of this latter tube a piece of hard, combustion tubing is adapted, by means of caoutchouc tubing. This hard tubing, which should be about 1 cm. in diameter, is

FIG. 54.



narrowed by drawing it out in the flame at intervals of about 2 cm., so as to present the form of a narrow tube, with 3 or 4 bulbs or wider portions on it (fig. 54, *b*).

The end of this tube is made slightly rough with a file, dipped into a solution of platinum tetrachloride, and heated; a thin coating of platinum is thus formed on the surface of the

* If red corks or tubing be employed they must be boiled in caustic soda and washed with water before being used, as they contain antimony, and generally a little arsenic sulphide.

tube, which prevents the glass fusing when the issuing hydrogen is ignited.

The hydrogen is most conveniently prepared by the action of dilute sulphuric acid upon zinc. For this purpose a quantity of granulated zinc is placed in the flask, and water added ; the whole apparatus is then put together, and a very little sulphuric acid poured into the flask by means of the funnel-tube. The hydrogen thus generated is dried by passing over the calcium chloride. After a little time, and when a sample of the gas tested in the usual manner (see Lesson II.) is shown to be free from air, the low flame of a Bunsen lamp is applied to the first bulb of the reduction tube, and the evolution of hydrogen maintained for about fifteen minutes. If after this time not the least trace of a metallic-looking mirror is formed in the tube beyond the heated portion, we may conclude that the materials are free from arsenic.

We are now ready to begin the actual examination of the liquid supposed to contain arsenic. It will generally be necessary to disconnect the apparatus, pour off the acid liquid from the zinc, add a little more water, and then a few drops of conc. sulphuric acid. After ascertaining that the issuing hydrogen is free from air, light it, and now apply a flame to the first bulb of the reduction tube ; when this is strongly heated, pour about one-half of the suspected liquid prepared as directed (p. 193) gradually down the funnel tube ; the evolution of gas increases, and if arsenic is present a metallic mirror is formed between the heated portion and the outlet of the reduction tube. If the evolution of arseniuretted hydrogen is considerable, part of it will probably escape decomposition by the heat applied ; the flame at the end of the tube will change to a peculiar bluish-white tint ; at the same time white fumes of arsenious oxide will appear immediately above this flame. Having obtained two mirrors in the reduction tube, remove the lamp, and bring a piece of cold porcelain, *e.g.* a small basin or crucible

lid, close to the end of the tube, so that the flame of the burning gas strikes against it. A brownish-black lustrous spot is produced on the porcelain.

Now extinguish the flame ; adapt a bent tube to the end of the delivery tube, and pass the gas into a solution of silver nitrate in a small test-glass. The liquid in the glass gradually blackens, metallic silver being deposited, while the solution contains arsenious acid ($6\text{AgNO}_3\text{Aq} + \text{AsH}_3 + 3\text{H}_2\text{O} = 6\text{HNO}_3\text{Aq} + 6\text{Ag} + \text{AsH}_3\text{O}_3\text{Aq}$).

The following precautions must be attended to in using these tests :—

1. A small quantity only of the acid liquid is to be poured at a time into the generating flask, otherwise the reaction will get very violent, and the contents of the flask will probably froth over ; the flask must not get hot.

2. The porcelain dish used for obtaining spots must be clean, dry, and at the temperature of the air. It must not be held for any length of time in the flame, but merely brought down upon the flame and withdrawn, otherwise the porcelain will become so heated that the arsenic spot will be vapourised.

3. Conduct the entire operation in a place where there is sufficient draught to carry off all arsenical fumes, as these are extremely poisonous.

If the process described for preparing the liquid to be tested for arsenic has been carefully performed, the presence of antimony in this liquid is almost impossible. As antimoniuiretted hydrogen, however, gives reactions very similar to those of arseniuiretted hydrogen, we must make sure that the mirror, spots, &c., are really due to the presence of arsenic.

(a) The mirror on the reduction tube, if caused by arsenic, is all deposited *after* the point at which the flame was applied, *i.e.* between the heated point and the outlet of the reduction tube.

Antimony being less easily vapourised than arsenic, is

* The liquid in the flask must not be allowed to get hot, otherwise H_2S will be produced, and will act on the arsenious oxide, converting it into the corresponding sulphide.

deposited *on both sides* of the heated spot. The arsenic mirror is lustrous, brownish-black in colour, and when in thin layers, and viewed against a sheet of white paper, is transparent. The antimony mirror when thus viewed appears as a brownish-black dust. Near the heated spot it is partly fused to small globules, and is almost silver-white in colour. That part of the tube containing the mirror is now to be cut off with a file, and reserved for examination.

(*b*) The spots on porcelain, if caused by arsenic, are lustrous; if caused by antimony, they have a velvet-like appearance, and are nearly black in colour.

If the arsenic spots are touched with a drop of sodium hypochlorite, free from chlorine, they are dissolved, while antimony spots are unaffected by this reagent. If the spots are touched with a drop of yellow ammonium sulphide, and heated gently over a flame, they are dissolved. On now evaporating off the excess of ammonium sulphide by gently heating and blowing, a yellow residue remains if the spot was arsenic; if antimony, the residue is orange. (A very good way of applying this reaction is to use a small wash-bottle, the blowing tube of which passes into a little conc. ammonium sulphide, while the exit-tube is cut off immediately below the cork; by this means a current of ammonium sulphide gas may be directed upon the spot; if arsenic, a yellow ring of arsenious sulphide (As_2S_3) is formed at the outer margin of the spot; if antimony, this ring is orange-red in colour; these rings disappear on continuing the passage of ammonium sulphide vapour over them; but reappear on gently breathing upon them.)

(*c*) If the gas was arseniuretted hydrogen, the silver nitrate solution through which the gas has been passed contains metallic silver and arsenious acid (see p. 190), along with excess of silver nitrate. On filtering from the silver precipitate, and carefully neutralising the filtrate with ammonia (adding, if necessary, a little more silver nitrate), a yellow precipitate of silver arsenite (Ag_3AsO_3) is ob-

tained. If the gas was antimonuretted hydrogen, the precipitate in the silver nitrate solution will contain all the antimony combined with silver ($3\text{AgNO}_3\text{Aq} + \text{SbH}_3 = 3\text{HNO}_3\text{Aq} + \text{Ag}_3\text{Sb}$). On filtering, therefore, and adding ammonia, no precipitate will be obtained; but if the precipitate is washed with hot water, then boiled with a concentrated solution of tartaric acid, and the insoluble part removed by filtration, an orange precipitate of antimonious sulphide is obtained on acidulating the filtrate with hydrochloric acid and passing sulphuretted hydrogen through it.

The part of the combustion-tube on which the mirrors are formed is cut off, and one-half of it sealed up in a small tube, and preserved as a *corpus delicti*, the other half is placed in a clean, dry, wide test-tube, and gently heated; the arsenic volatilises, is oxidised, and deposited as arsenious oxide on the wider tube, in the form of a white crystalline ring. The little bit of combustion-tube is thrown out from the test-tube, the arsenious oxide dissolved in water, this solution divided into two parts, and tested (1) with ammonio-silver nitrate (2) with ammonio-cupric sulphate (see p. 114 (*b*) and (*c*)). These tests taken together furnish conclusive evidence of the presence of arsenic.

2.—*Method of Fresenius and von Babo*.—This process depends upon the fact that arsenious sulphide, when fused with potassium cyanide and sodium carbonate, is readily reduced, metallic arsenic being formed. The delicacy of the reaction is increased by heating the mixture in a slow current of carbon dioxide.

Fig. 55 shows the arrangement of the apparatus.

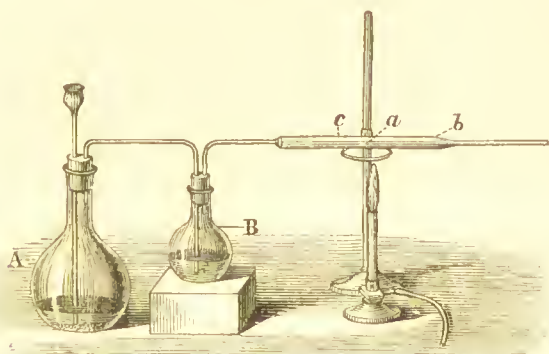
A is an apparatus for producing the carbon dioxide; B is a bottle containing conc. sulphuric acid, which dries the carbon dioxide; C is a piece of hard glass tube, about 7 mm. bore and 30 cm. long.

The liquid obtained, as described on p. 193, is diluted with water and saturated with sulphuretted hydrogen gas, with attention to the directions already given. The resulting

precipitate is washed, and excess of sulphur removed by treatment with carbon disulphide; the residue, after being again washed, is dissolved in ammonia, and the solution evaporated to dryness on the water-bath.

About *one-half* of the dry arsenious sulphide thus obtained is mixed with ten times its weight of a mixture of 3 parts perfectly dry sodium carbonate and 1 part dry potassium cyanide. The powder is placed in a little piece of stout paper with turned-up edges, which is pushed into the

FIG. 55.



reduction-tube to *a*; the tube is now turned half round on its axis, so that the powder falls out of the paper, which is then withdrawn. Pass a slow current of carbon dioxide through the tube, heating it gently along its whole length until *perfectly dry*. The gas should now be passing through *B* at the rate of one bubble per second; heat the tube at *b* to redness, and apply the flame of a second lamp to the mixture, proceeding from the end nearest *B* to the point at which the mixture is situated. The arsenic is gradually expelled and condenses, chiefly at *b*; the very small quantity which escapes may be recognised by its garlic odour. By advancing the second lamp slowly towards the first, all the arsenic is driven into the narrow portion of the tube,

The tests mentioned on page 198 may be applied to this mirror. By this process no mirror is obtained from any antimony compound.

If in the preliminary examination of the animal matter small pieces of solid matter, which appear like arsenious oxide, have been obtained (page 190), they may be examined in the following way :—

A small particle is introduced into the narrow portion of a reduction-tube (fig. 56), and a thin splinter of freshly heated charcoal is dropped upon the top of it. That part of the tube where the charcoal is situated is heated to redness over a very low flame, and the tube gradually moved until the supposed arsenious oxide is also heated. If it vapourises, and forms a brownish-black lustrous ring above the charcoal, the substance is, in all probability, arsenious oxide. To make certain, heat the arsenical mirror ; it vapourises, is oxidised, and again condenses on the wider portion of the tube, in the form of a white crystalline sublimate. This is dissolved in water, and tested as directed on p. 198.



Another fragment of the white substance, supported on asbestos, is brought into the reducing Bunsen flame, and metallic films obtained on porcelain (p. 98) ; these are tested with sodium hypochlorite and ammonium sulphide, as already directed.

The several residues which you have set aside during the process must now be examined.

1. Residue A is to be examined for lead, mercury, and antimony ; it is dissolved in aqua regia, any insoluble matter being removed by filtration ; the solution is boiled down to a small bulk, hydrochloric acid added, and the liquid again evaporated ; it is then diluted with water, and saturated with sulphuretted hydrogen gas (see p. 191). Any precipitate which may form is collected, washed, heated with ammonium sulphide (see p. 192), and the insoluble

portion separated by filtration. The solution is neutralised with acid ; if an orange-coloured precipitate forms, it is collected, washed, and tested by the dry tests for antimony (see p. 115). The portion insoluble in ammonium sulphide is well washed and boiled with dilute nitric acid, &c., as directed for the separation of mercury and lead, on page 161.

2. Residue C is to be examined for mercury, lead, and copper.

The filter is perforated, and the precipitate washed with the smallest possible quantity of water into a little conical glass ; moderately concentrated nitric acid is added, and a gentle heat applied. If the precipitate entirely dissolves, mercury cannot be present. If anything remain undissolved, pour off the liquid into a small porcelain basin, wash the insoluble matter by decantation (adding the washings to the liquid in the basin), and dissolve it in aqua regia ; to this solution apply the copper foil and stannous chloride tests for mercury (see I. (*b*) and (*c*), p. 111).

The nitric acid solution is evaporated on the water-bath almost to dryness. After addition of *pure* sulphuric acid, water is added, and after gentle heating the liquid is decanted off from any white solid matter (lead sulphate). This is transferred to a conical glass, and washed several times by decantation ; the liquid and washings being preserved. A conc. solution of sodium carbonate is now added, and allowed to stand in contact with the precipitate for several hours, with frequent stirring ; a little water is then added and nitric acid until a clear fluid is obtained. The presence of lead in this liquid is confirmed by testing a portion with potassium chromate, and another portion with potassium iodide (see III. (*c*), p. 110). The liquid decanted from the insoluble lead sulphate is concentrated and tested for copper by adding ammonia to one portion and potassium ferrocyanide to another (see III. (*b*) and (*c*), pp. 112, 113).

3. Residue D may contain antimony ; it is dried, removed from the small filter, which is incinerated, and the ash placed

along with the residue in a porcelain crucible, and fused with potassium cyanide. After cooling, the mass is washed into a porcelain dish, water is added, the washings poured off, and the residue in the dish examined for small metallic globules. If these are found they are heated with a little aqua regia, whereby they are dissolved, fumes being copiously given off. Boil down the solution to drive off nitric acid, dilute with water, and pass sulphuretted hydrogen through a part of the liquid. An orange-coloured precipitate shows antimony. The other part of the liquid is introduced into Marsh's apparatus, and examined for antimony (see pp. 196 and 197).

There now remains only the precipitate by ammonium sulphide (p. 192), which may contain zinc. Acetic acid is added to the liquid in which the precipitate has formed. After a little time the precipitate is collected, washed, dried, and heated to redness. The residue is dissolved in sulphuric acid, with a little hydrochloric or nitric acid, the liquid is freed from excess of acid by evaporation and diluted, and to this solution the usual tests for zinc are applied (see p. 124).

B. *ORGANIC POISONS.*

By the method to be described the suspected matter may be tested for hydrocyanic acid, oxalic acid, and the alkaloids, without introducing any substance capable of interfering with the subsequent tests applied for the detection of the metallic poisons.

I. *HYDROCYANIC ACID.*—This acid being very volatile, cannot be detected in the stomach, intestines, &c., unless these be subjected to examination soon after death.

The evidence of hydrocyanic acid is generally found in the stomach, intestines, or vomited matter : if not found in any of these it is almost fruitless to search for it in the liver and urine. Its presence has been traced in the brain, spinal marrow, and heart, by the peculiar odour which it possesses.

The first test is the odour emitted by the poison : this resembles oil of bitter almonds. Particular attention should always be paid to this point.

Whether the odour of hydrocyanic acid has been detected or not, it is necessary to proceed with the further examination. The method is based upon the fact that when the matter containing the poison is acidified and distilled, the distillate contains all, or almost all, the hydrocyanic acid. If, however, cyanides, even the non-poisonous ferro- or ferricyanide of potassium, be present, hydrocyanic acid will be found in the distillate obtained according to this method. A special examination is, therefore, necessary in order to determine in what form the cyanogen compound originally existed. This examination we shall refer to at a later stage.

The solid matter is cut into shreds, mixed with distilled water, so as to form a thin cream or paste, and, if the reaction be not strongly acid, tartaric acid is added in solution ; the whole is then transferred to a retort connected with a condensing apparatus, and gently heated in a calcium chloride bath until 20 c.c. or so have passed over. In this distillate hydrocyanic acid, if present, may be detected by the following tests :—

(a) To a part of the distillate a few drops of ferrous sulphate solution and one drop of ferric chloride solution are added, together with a little caustic soda ; a bluish-green precipitate forms, consisting of a mixture of Prussian blue and ferric hydrate ; on adding hydrochloric acid, the ferric hydrate dissolves, leaving a blue precipitate, or, if but very small quantities of the poison are present, a blue-coloured solution, from which a slight precipitate separates after some time.

(b) Before applying this test a very small quantity of the distillate is tested with a drop of ferric chloride ; if no red colour is thereby produced—showing the absence of acetates, formates, or meconic acid—a further portion of the distillate

is mixed with a few drops of yellow ammonium sulphide, and evaporated at a gentle heat until it has become colourless. Ammonium sulphocyanide is thus formed, which, on acidifying with hydrochloric acid, and adding a drop of ferric chloride, gives a deep red colour (see XV. (c), p. 146.)

In applying this test to very small quantities of a fluid, it will be found advisable to place the liquid in a watch glass, over which is inverted a second watch glass, in which a drop of yellow ammonium sulphide has been placed. The lower glass is very gently heated for ten or fifteen minutes, the upper glass is then removed, heated very cautiously, until the liquid which it contains is perfectly colourless, and then one drop of pure hydrochloric acid and a drop of ferric chloride added.

(c) Another very good test for small quantities of hydrocyanic acid consists in immersing in a portion of the distillate a small slip of filtering paper, previously soaked in tincture of guaiacum, dried, and moistened with water containing a small quantity of copper sulphate.* The paper is coloured blue if hydrocyanic acid is present.

If the presence of this acid has been proved in the distillate we must institute further experiments to determine whether ferro or ferricyanide of potassium exists in the original substance. For this purpose mix a quantity of the original substance with water, filter, acidulate the filtrate with hydrochloric acid, and to one half add ferric chloride, to the other ferrous sulphate; the formation of a blue precipitate indicates, in the first case ferro, in the second ferricyanide of potassium. If one or both of these double cyanides have been proved present, there yet remains another problem to be solved, viz.: Did the original matter contain both the non-poisonous cyanide and also the poisonous hydrocyanic

* These papers are prepared by immersing good filtering paper in a solution of 3 parts tincture of guaiacum in 100 parts rectified spirits and drying. Just before use, moisten the papers in a solution prepared by dissolving 1 part cupric sulphate in 500 parts of water.

acid or poisonous cyanide? Otto recommends the following process: The mass is mixed with a solution of ferric chloride, Prussian blue is thus formed if ferrocyanide be present; sodium carbonate is added to alkaline reaction, then tartaric acid, until the mass is slightly acid, and the whole distilled. If hydrocyanic acid, or a poisonous cyanide were originally present, the acid will be found in the distillate, but if potassium ferrocyanide only were present, no trace of the acid will be detected.

II. OXALIC ACID.—In searching for this poison it is generally necessary to examine not only the stomach, intestines, &c., but also vomited matter, and, if possible, the urine and blood; because the acid being rapidly absorbed by the system, quickly finds its way from the stomach into the heart and veins, unless partially ejected in the vomit.

The process for the detection is as follows:—

The substance to be examined is boiled with distilled water in a large porcelain dish, and the liquid filtered while hot; the residue is again boiled and filtered, the two filtrates united and evaporated to dryness at a gentle heat, the residue repeatedly treated with small quantities of cold absolute alcohol, and lastly the alcoholic liquid evaporated to a small bulk and allowed to crystallise. (If much organic matter be present in this solution it should be precipitated by tincture of gall nuts—previously tested for oxalic acid—and filtered.) The crystals which form are dissolved in water, and the proper tests for oxalic acid applied to the solution.

The residue remaining after treatment with absolute alcohol—as first described—must also be tested for oxalic acid, as it may contain traces of this acid undissolved by the alcohol: or if an alkaline oxalate were the poison used, it will be found here. This residue is treated repeatedly with small portions of cold water, and the resulting liquid precipitated with calcium chloride; the precipitate is collected, washed, and boiled for half an hour or so with a solution of potassium carbonate, the resulting soluble potassium oxalate

is separated by filtration from the calcium carbonate, lead acetate is added to the filtrate, and the precipitate which forms is collected and washed ; it is then suspended in water through which a current of washed sulphuretted hydrogen is passed ; after the liquid is thoroughly saturated with the gas the insoluble lead sulphide is separated by filtration, and the filtrate evaporated until the acid crystallises out. The crystals are dissolved in water and the tests for oxalic acid applied to the solution.

Sometimes antidotes may have been administered in cases of poisoning by oxalic acid ; those usually employed are magnesia or a lime salt. In such instances the detection of the acid becomes a matter of considerable difficulty. The mass remaining after boiling with water is washed with water in a large dish, the heavier particles being thus separated as far as possible from the comparatively light organic matter. The impure oxalate is collected and treated with hydrochloric acid—if magnesia was the antidote employed ; with moderately concentrated nitric acid—if lime has been used. The solution is filtered, and saturated with ammonia ; if a precipitate forms (calcium oxalate) it is digested with acetic acid to remove traces of calcium phosphate, and then treated with potassium carbonate, &c., as already described. If no precipitate forms on addition of ammonia, potassium carbonate is added, the resulting magnesium carbonate collected on a filter, and the filtrate treated with lead acetate, &c.

III. ALKALOIDS. — All the more commonly occurring alkaloids may be detected by the following processes :—

Method A.—Process of Stas, modified by Otto.

The suspected matter is heated to 70° or 75° with twice its weight of conc. alcohol, and acidified with one or two grammes of tartaric or oxalic acid.

Filter when cold, wash with conc. alcohol, and add the washings to the filtrate. Evaporate the liquid, either under

a bell jar over conc. sulphuric acid, or in a retort through which a current of air is drawn by means of the filter pump.

If fatty or insoluble matter separates during this process, remove it by filtration, and continue to evaporate the liquid nearly to dryness. Digest the residue with *cold absolute* alcohol, filter, wash the residue with alcohol, and evaporate the filtrate to dryness in *vacuo*, or spontaneously in the air. Dissolve the residue in the smallest possible quantity of water, and shake this solution with ether repeatedly, so long as the ether becomes coloured and yields a residue on evaporation ; add now acid sodium carbonate so long as effervescence ensues, again add 4 or 5 volumes of ether, shake up well, and allow to stand. Transfer a small quantity of the ethereal liquid to a watch glass and allow it to evaporate spontaneously. If oily drops are left, which emit a pungent odour when heated, volatile bases are probably present ; if a solid residue, or a turbid fluid with solid particles suspended in it remain, a non-volatile base must be looked for.

If it is necessary to search for a volatile base, add to one half of the mixed ethereal and aqueous solutions 1 or 2 cb. cm. of conc. caustic potash solution, and shake well ; the base is thus liberated and is dissolved by repeated treatment with ether, which must be continued until the lower portion leaves no residue on evaporation. Dilute sulphuric acid is now added to the ethereal solution to *decidedly* acid reaction ; shake well, and after decanting the supernatant ether, again treat the aqueous fluid with dilute acid.

The aqueous solution now contains the bases, nicotine, picoline, and the greater part of the conine, if present, as sulphates. By addition of conc. caustic potash in excess, and subsequent treatment with ether, these bases are again liberated and dissolved, and on evaporating the ethereal liquid (best *in vacuo* over sulphuric acid) they are obtained in the residue. Ammonia is removed by this evaporation.
Call this Residue A.

From the second half (or from the whole if no volatile

bases are present) of the mixture of aqueous and ethereal solutions, the ether is decanted and allowed to evaporate. The residue is dissolved in a small quantity of water acidulated with sulphuric acid, the solution shaken repeatedly with ether, and the ether removed (animal or fatty matter is thus got rid of). Sodium carbonate is now added in excess to the aqueous solution, and the liquid again shaken with ether; the resulting ethereal liquid, on spontaneous evaporation, yields the non-volatile bases nearly pure. *Call this Residue B.*

Method B. Process of Uslar and Erdmann.

This process is more suited for the detection of non-volatile alkaloids. The suspected matter, mixed with water to the consistence of a thin paste, and acidified with dilute hydrochloric acid, is heated for several hours to 70° or 80° then strained through moistened linen, the residue washed with hot acidulated water, and the washings added to the filtrate. The liquid is now saturated with ammonia and evaporated to dryness. By the addition of a little pure sand the residue is easily reduced to powder. Boil the powder repeatedly with amyl alcohol, and filter while hot. To the alcoholic solution, transferred to a cylinder, add ten volumes of almost boiling water, acidify with hydrochloric acid, and shake the mixture vigorously; the alkaloids—as hydrochlorides—pass into the aqueous solution while the amyl alcohol retains the fatty matter. The latter is removed by a pipette, and the acid solution again shaken with amyl alcohol to remove the last traces of colouring matter. By concentrating, treating with ammonia, and repeated shaking with hot amyl alcohol, the bases will be obtained in the alcoholic solution nearly pure.

If any further purification is required, the residue is redissolved in hydrochloric acid, after removal of the amyl alcohol by evaporation on the water bath; the liquid is

shaken with alcohol, the latter drained off, and ammonia added, &c., as described. The residue, after removal of the alcohol, contains the pure alkaloids—a small portion of it should yield no brown colour with a drop of conc. sulphuric acid.

We now proceed to the further testing of the several residues.

Residue A (p. 207) contains the volatile alkaloids.

The presence of conine or nicotine in this residue will be made manifest by its odour, that of the former being very strong and penetrating, and that of the latter ethereal and tobacco-like. The odour of picoline is also very characteristic; when inhaled through the nostrils the vapour of this substance produces a bitter taste in the mouth and back of the throat. On the addition of water to this residue, nicotine, if present, dissolves, while picoline or conine remains insoluble. If, therefore, oily drops form on the surface of the water, one or other of the latter alkaloids is present. If no such drops form, nicotine must be sought for.

To distinguish between conine and picoline, add to small quantities of the oily liquid on watch glasses—

1. Conc. nitric acid. A blood-red colour shows the presence of CONINE.

2. Solution of albumen. It is coagulated by CONINE.

3. Add a few drops of hydrochloric acid, and evaporate gently, then add platinum tetrachloride. If a yellowish crystalline precipitate forms, PICOLINE is present; but if this precipitate is produced only on addition of alcohol, CONINE is present.

To distinguish between nicotine and picoline; mix small quantities of the aqueous solution in watch glasses with—

1. Hydrochloric acid and platinum tetrachloride. A precipitate indicates NICOTINE; if, however, the precipitate only forms upon evaporation, this shows the presence of PICOLINE.

2. Tincture of iodine added to solution of NICOTINE gives

a yellowish turbidity, which disappears after a little time ; but on further addition of the reagent a copious kermes-coloured precipitate separates, which also disappears upon standing.

Residue B (p. 208) contains the non-volatile alkaloids. Generally the examination is limited to a search for one particular alkaloid. Of these, which may be here detected, we shall notice morphine, narcotine, brucine, strychnine, veratrine, colchicine and aconitine. If we are searching specially say for strychnine, then the tests for this alkaloid are to be at once applied to a portion of the crystalline residue. If, however, we possess no clue to the nature of the alkaloid present, we must place several fragments of the residue in small clean porcelain dishes, and apply the following tests :—

1. 4 or 5 drops of *pure conc.* sulphuric acid.

A yellow colour changing to red or violet indicates
VERATRINE OR ACONITINE.

A bluish-violet or yellow, changing on heating to cherry red, indicates NARCOTINE.

A rose colour changing to yellow indicates BRUCINE.

A yellow-brown colour indicates COLCHICINE.

Add now to the fluid obtained as above—

2. 10 or 20 drops conc. sulphuric acid containing nitric acid,* after 20 to 30 minutes if there ensues

A violet colouration, it indicates MORPHINE.

STRYCHNINE is not coloured by any of these reagents.

From these tests an indication as to which alkaloid is present will have been obtained. Confirmatory tests must now be applied. The following are very good :—

I. VERATRINE ($C_{32}H_{52}N_2O_8$).—

Conc. sulphuric acid at first causes this alkaloid to form into small lumps ; these, however, speedily dis-

* Three drops of conc. nitric acid are mixed with 100 c.c. of water, and ten drops of this liquid added to 40 c.c. of pure conc. sulphuric acid.

solve to a light yellow fluid, changing to reddish yellow, and eventually to blood red.

Conc. hydrochloric acid forms a colourless solution, which becomes intensely red by long-continued boiling. This reaction is very delicate.

II. ACONITINE ($C_{30}H_{47}NO_7$).—

Sulphuric acid produces a yellow colour changing to violet.

Nitric acid dissolves it without colour.

III. NARCOTINE ($C_{22}H_{23}NO_7$).—

The reaction already given is the most delicate for this alkaloid. The changes of colour are marked, at first a bluish violet (or in less pure specimens a yellowish colour) is produced. On gently warming, the colour changes to orange-red, bluish stripes then appear; if the heating is now discontinued the liquid becomes cherry-red as it cools, but by continuing the application of heat a deep violet-red is formed.

IV. BRUCINE ($C_{23}H_{26}N_2O_4$).—

Conc. nitric acid yields a very red fluid, becoming yellow when heated, and changing to intense violet on addition of stannous chloride or ammonium sulphide.

Conc. sulphuric acid (4–5 drops) produces a faint rose-colour, changing to yellow; 10–20 drops of sulphuric acid mixed with nitric acid (see note, p. 210) being now added, a transient red colour, changing again to yellow, is produced.

V. COLCHICINE ($C_{17}H_{19}NO_5$).—

Conc. nitric acid gives a deep violet or blue colour, changing to olive-green and yellow.

Tincture of iodine throws down a kermes-coloured precipitate.

Tannic acid gives a white precipitate, soluble in alcohol and acetic acid.

VI. MORPHINE ($C_{17}H_{19}NO_3$).—

The test already mentioned, viz., the formation of a violet colour upon addition of sulphuric acid followed by a mixture of the same acid with nitric acid, is characteristic.

If a few small pieces of manganese dioxide are added to the liquid obtained as above, it changes to mahogany colour.

If solid morphine or a morphine salt is moistened with a solution of 1 part of iodic acid in 15 parts of water, and a solution of 1 part of starch in 400 of water is added, a blue colour is produced. If now a layer of very dilute ammonia is poured on this blue liquid, two coloured rings are formed at the point of contact, the upper blue, the lower brown. This reaction serves to detect $\frac{1}{20,000}$ th part of morphine (*A. Dupré*).

A neutral concentrated solution of a ferric salt gives a deep blue colour with salts of morphine.

VII. STRYCHNINE ($C_{21}H_{22}N_2O_2$).—

Strychnine and its salts have an *intensely bitter* taste.

A colourless solution of this alkaloid in *pure* sulphuric acid shows a splendid bluish colouration, changing to wine-red and then to reddish-yellow, on addition of the following oxidising agents :—

1. A very small quantity of solid manganese dioxide.
2. A crystal of potassium chromate.
3. A crystal of potassium permanganate.

The action of the two last reagents is very marked. The small fragment of the oxidiser used should be pushed about the dish with a glass rod.

If morphine be present it interferes with these reactions, and must therefore be removed. To do this, add potassium chromate to the concentrated *aqueous* solution, and filter (the morphine is found in the filtrate) ; wash the precipitate slightly, dry it, and mix it in a watch

glass with a few drops of conc. pure sulphuric acid ; the blue violet colour is immediately produced.

The following are a few special methods for the testing of certain alkaloids.

I. QUININE ($C_{20}H_{24}N_2O_2$).

The acid salts of this alkaloid exhibit *fluorescence* in a remarkable degree.

Tests. Chlorine water with subsequent addition of ammonia gives an intense emerald-green colour. If the addition of ammonia be preceded by that of a few drops of a solution of potassium ferrocyanide, a red tint is produced, soon turning to a dirty brown.

Bromine vapour may be advantageously substituted for chlorine in the above reactions (*Flückiger*).

Medicinal *sulphate of quinine* often contains as impurities small quantities of the sulphates of cinchonine and quinidine. To detect these, the method of *Liebig* as modified by *Stoddart* is employed : .6 gm. of the suspected salt is dissolved in about 10 drops of pure dilute sulphuric acid, with the addition of 50 or 60 drops of distilled water in a small stoppered bottle ; 150 drops of pure ether, mixed with 3 drops of alcohol and 40 drops of a solution of caustic soda (1 to 12 of water), are now added. After brisk agitation the bottle is set aside for 12 hours, when the smallest traces of quinidine or cinchonine, if present, may be seen separating out at the line of separation of the two liquids in the bottle.

DETECTION OF STRYCHNINE IN BEER (Graham and Hofmann). One gallon of the beer is shaken with 4 ounces of animal charcoal, and after standing 12 hours the latter is collected and washed once or twice with cold water, then boiled with alcohol, the alcoholic solution evaporated to dryness at a gentle heat, the residue shaken with a few drops

of caustic potash and ether, the ethereal solution evaporated, and the residue tested for strychnine by the usual methods.

DETECTION OF ADMIXTURE OF BRUCINE WITH STRYCHNINE.—The presence of brucine in samples of strychnine may be detected by the intense red colour imparted to the nitric acid solution of the suspected salt when the former alkaloid is present.

DETECTION OF OPIUM.—As opium contains meconic acid ($C_7H_4O_7$) in addition to morphine, it is necessary to obtain the tests for this body before deciding whether a given sample actually does or does not contain opium.

Meconic Acid.

1. Ferric chloride produces a deep red colouration, unaltered by boiling or treatment with mercuric chloride.

2. Lead acetate precipitates white lead meconate, insoluble in acetic acid.

To prove the presence of opium in organic tissues, &c.: evaporate the suspected matter to dryness on the water-bath, and digest with water containing a little acetic acid for some time; filter, and add lead acetate to the filtrate, warm and again filter after cooling. From the filtrate, excess of lead is removed by means of sulphuretted hydrogen, the clear liquid evaporated to dryness, a little potassium carbonate added, and the mixture shaken with an ethereal solution of acetic ether; this solution will now contain the morphine, which may be tested for according to VI. p. 210.

The precipitate produced by lead acetate is suspended in water, through which a current of sulphuretted hydrogen is passed, the resulting lead sulphide removed by filtration, excess of sulphuretted hydrogen driven off by heat (the temperature must not exceed 70° C.), and the concentrated liquid tested for meconic acid.

IDENTIFICATION OF BLOOD STAINS.

If the stains occur on undyed cloth, linen, or cotton, the stained piece is cut out, and suspended in pure water until the stain is almost entirely removed. To the solution thus obtained various tests are applied.

1. On heating, the red or reddish-brown colour disappears, while small particles of coagulated albumen are seen floating about the liquid ; these disappear on addition of caustic soda.

2. A solution of tannin gives a white precipitate.

3. A portion evaporated in a porcelain dish leaves a brown lustrous coating which, on treatment with chlorine water and subsequent evaporation, becomes colourless. If a few drops of water and a very little potassium sulphocyanide are now added a reddish colour is produced, owing to the iron in the blood.

4. A small quantity of tincture of guaiacum mixed with an ethereal solution of hydrogen peroxide, gives a *blue colour* (this colour is produced with other substances than blood).

5. Another part of the stained material is boiled with glacial acetic acid, a little sodium chloride being added during the ebullition ; a few drops are then evaporated to dryness at from 40° to 60° , and the residue examined under the microscope for hæmin crystals. This compound forms rhombic crystals, or sometimes six-sided plates, dark blue by reflected, dirty brown by transmitted, light. If the stain occurs in soil or on iron, the dried soil, or the part scraped off the iron, must be heated with weak potash ley, and chlorine water added to the filtered solution. A coagulum is thus formed which yields hæmin crystals on treatment with salt and glacial acetic acid. Some observers say that the hæmin crystals from the greater number of warm-blooded animals are identical ; while, according to others, those obtained from human blood differ essentially from all others.

Blood gives very characteristic absorption bands with

the spectroscope. The process, with a description of the instruments, &c., to be employed, and of the results obtained, will be found fully described in a series of papers by Mr. H. C. Sorby, in the *Chem. News*, vol. xi., 1865.*

SECTION V.

EXAMINATION OF URINE AND URINARY CALCULI.

THE number of substances contained in healthy urine is very great ; for the purpose of qualitative examination they may be roughly classed as follows :—

1. Water. 2. Inorganic substances—Potassium, sodium, calcium, magnesium, and iron, existing as chlorides, phosphates, sulphates, nitrates, carbonates, or silicates. Ammonia also occurs in small quantities. 3. Organic substances.—

a. Nitrogenised ; urea, uric and hippuric acids ; creatinine and xanthine ;—*b.* Non-nitrogenised ; lactic, succinic, oxalic, formic, and phenylic acids, and sugar (?). 4. Colouring and extractive matter, and more or less mucus in suspension.

In addition to these, small quantities of many other substances are found in healthy urine, while in cases of disease there may be present—blood, albumen, fibrine, fats, cystine, glucose, &c. The reaction of the urine should be first ascertained by test-papers ; healthy urine has generally an acid reaction, but immediately

after meals it may be neutral or even slightly alkaline. The specific gravity of healthy urine varies from 1.015 to

FIG. 57.



* See also article 'Hæmoglobin,' in *Watts' Dictionary of Chemistry* (2nd ed.), vol. ii., especially p. 663. Compare also MacMunn, *The Spectroscope in Medicine* (1883), pp. 130-148.

1.020. This is determined by means of the urinometer (see fig 57), which consists of a glass bulb, containing mercury, to sink it in the liquid, furnished with a stem, graduated from 1,000 to 1,060. A sample of the urine, which should represent the average quality of the entire amount voided during twenty-four hours, is poured into a cylindrical glass, the urinometer floated in the liquid, and the number of degrees at the point where the surface of the urine is in contact with the stem, read off, and noted down. The urinometer is now depressed in the urine, and after coming to rest another reading is taken. A high specific gravity generally points to the presence of sugar, a low specific gravity is more frequently due to the ingestion of large quantities of liquid, but it is also caused by several diseases.

2. The odour, transparency, and colour of the urine must also be noted. If the colour is saffron-yellow, or inclining to brown, probably biliary matter is present; in this case a yellow scum forms on the surface on agitating the sample. If the urine is turbid this is probably due to the presence of fatty or chylous matter. A smoky-red colour is diagnostic of blood.

3. A quantity of the urine is allowed to stand for some time; if a sediment forms it is collected on a filter and reserved for examination.

4. The clear filtrate must now be tested for :

a. Albumen.—Heat the upper layer of a small quantity of the sample in a test-tube to the boiling point, the lower layer remaining cool; by now holding the tube against the light the slightest turbidity in the upper layer is easily detected. Allow a few drops of dilute nitric acid to flow down the tube into the urine. If the cloudiness is permanent it is due to albumen which has been coagulated by the heat; if the cloudiness disappears, it is due to the presence of earthly phosphates; no albumen is present. If the preliminary examination has shown that the urine has an alkaline reaction it

must be rendered slightly acid by the addition of a few drops of *acetic acid* before testing for albumen.

In the event of albumen being detected, the whole of the urine, filtered from sedimentary matter, must be heated with the addition of a little acetic acid, filtered, and the filtrate tested for :

b. Urea and Uric Acid.—A portion of the sample is concentrated on the water-bath until it is of the consistence of a syrup. After the liquid is cold, nitric acid (free from nitrous acid) is gradually added ; the formation of delicate rhomboidal crystals of nitrate of urea, which are best seen under the microscope, tells us that urea is present.

Another portion of the sample, placed in a beaker glass, is acidulated with hydrochloric or acetic acid, and allowed to stand for 30 or 40 hours. If reddish-brown crystals form on the sides or bottom of the glass they are removed and heated with nitric acid ; reddish-coloured fumes are evolved, while the nitric acid solution, when evaporated to dryness, gives, on the addition of strong ammonia water, a magnificent purple colouration. These reactions are indicative of uric acid. (The colouration is caused by the formation of murexide, $C_8N_6H_8O_6$.)

c. Hippuric Acid ($C_9H_9NO_3$).—A quantity of the urine is evaporated to about the third of its volume on the water-bath, and allowed to cool. If a crystalline precipitate forms it may contain calcium hippurate (in addition to other substances). This acid occurs in very small quantities in urine ; as its clinical import is not clearly known, further details of its detection are unnecessary.

Chlorides, phosphates, and sulphates are also present in healthy urine. Their presence is recognised by the usual tests.

The above-mentioned substances, with the exception of albumen, are normal constituents of urine ; we now proceed to test for certain substances found in abnormal urine.

a. AMMONIUM CARBONATE.—A quantity of the clear

filtered urine is treated with hydrochloric acid ; effervescence ensues. Another portion is boiled with caustic potash, when ammonia is disengaged.

b. SUGAR.—Prepare a little of Fehling's copper solution by dissolving 3 grams of pure dry copper sulphate crystals in 20 c.c. of water, and adding gradually a solution of 1·5 grams of crystallised sodium-potassium tartrate in 6 c.c. of caustic soda solution (sp. gr. 1·14). This solution must be kept in a blue stoppered bottle.

Heat a few cubic centimetres of this solution to boiling in a test tube, and gradually add the sample of urine drop by drop ; if a red precipitate falls down (cuprous oxide, Cu_2O) sugar is present. Before using this solution it must be heated to boiling and carefully examined ; if any precipitate forms the solution is unfit for use—a new one must be prepared. The amount of urine added should not exceed the bulk of Fehling's solution used.

c. SULPHURETTED HYDROGEN.—This gas very rarely occurs in fresh urine ; its presence is recognised by its smell and its blackening action on slips of paper moistened with lead acetate.

The sedimentary matter which may have formed when the urine was allowed to stand at rest must now be examined. It may contain (*a*) uric acid, generally appearing as a granular precipitate varying in colour from light yellow to orange yellow and brown. (See reaction with nitric acid and ammonia, p. 218.)

d. URATES.—The sediment caused by urates (chiefly of sodium, potassium, calcium, and ammonium) varies in appearance from acicular crystals to irregular clot-like masses, hardly distinguishable from mucus or blood.

The sodium and potassium urates are soluble, the calcium and ammonium salts almost insoluble, in water. A drop of hydrochloric acid added to a sediment composed of urates sets free uric acid, which may be recognised under the microscope by its crystalline form, and by the formation of murexide when treated with nitric acid and ammonia.

e. CALCIUM OXALATE.—This forms a sediment, in which ‘dumb-bell’ shaped crystals are occasionally visible. Calcium oxalate is insoluble in acetic acid. After gentle ignition on platinum foil calcium carbonate remains, which effervesces on addition of an acid. Dissolve a little of the supposed calcium oxalate in nitric acid, and add mercurous nitrate, mercurous oxalate will be precipitated; this is removed by filtration, ammonia added to the filtrate to precipitate excess of mercury (existing as nitrate), and after another filtration oxalic acid is added, when a white precipitate of calcium oxalate is obtained.

f. MAGNESIUM - AMMONIUM PHOSPHATE, OR CALCIUM PHOSPHATE.—The former double phosphate occurs in large transparent rhombic prisms, the latter generally in an amorphous powder, but sometimes in small penniform, or acicular crystals. Dissolve the sedimentary matter in a little hydrochloric acid, add sodium acetate in excess, calcium oxalate, if present, is thus precipitated; filter, and to the filtrate add oxalic acid, which precipitates the calcium which originally existed as phosphate, again filter, and add to the filtrate ammonia in excess, when magnesium phosphate will be thrown down.

EXAMINATION OF URINARY CALCULI.

These calculi may be divided into groups according as they comport themselves when heated on platinum foil. Thus we have the following divisions:—

I. *Calculi which leave no fixed residue.*—These may be composed of uric acid, ammonium urate, or hippurate, xanthine, cystine, cholesterine, colouring matters of the bile, fibrine, or albumen.

II. *Calculi which leave a fixed residue.*—This group is subdivided into

a. *Those which are partially combustible.*—Sodium or

calcium urates, and calcium or magnesium phosphates, oxalates, or carbonates.

b. Those which are entirely fixed.—These must consist of mineral matter entirely.

Group I.—*Calculi which leave no fixed residue.*

A. A portion of the substance is heated with concentrated nitric acid, the resulting solution evaporated to dryness on the water-bath, and the residue moistened with one drop of strong ammonia water.

a. It is coloured purple-red.—Uric acid, or ammonium urate. Another small portion of the calculus is gently heated with caustic potash.

a. Ammonia is evolved.—AMMONIUM URATE.

β. No ammonia is evolved.—URIC ACID.

b. It is not coloured purple-red.

a. The nitric acid solution become *brown* during evaporation. The residue is soluble in ammonia, microscopic hexagonal tables being deposited from this solution.—CYSTINE.

Cystine when heated evolves a peculiar empyreumatic odour. The potash extract, when decomposed by a solution of lead oxide (PbO) in caustic potash, and heated, gives a precipitate of lead sulphide if cystine were present (*Liebig*). (Mucus, albumen, and other sulphur-containing compounds would, however, give a similar reaction.)

β. The nitric acid solutions become yellow during evaporation. The residue is amorphous, and insoluble in hydrochloric and oxalic acids.—XANTHINE.

B. A portion of the calculus is heated on platinum foil, It burns with a clear white flame.—CHOLESTERINE or FIBRINE.

a. If the calculus possesses a crystalline structure, dissolves in boiling alcohol, from which solution small

shining spangles are precipitated, and is insoluble in, and not saponified by caustic potash, it consists essentially of CHOLESTERINE.

- b.* If during combustion of the calculus the smell of burning horn is perceptible; if a portion of the calculus dissolves in caustic potash, and is precipitated from this solution by acetic acid, but is soluble in excess of this reagent, it consists chiefly of FIBRINE.

C. The calculus is of a brown colour, it is friable, and when burning the smell of calcined animal matter is perceptible. BILIARY ACIDS, OR COLOURING MATTER.

- a.* It is scarcely soluble in alcohol or water, but is dissolved (with a brown colour) by caustic potash. If, on adding to this solution an equal volume of alcohol, and then a little *fuming* nitric acid, the colour changes to green, then to blue, violet, and red, after some time again turning yellow, we conclude that BILIARY COLOURING MATTER is present.

- b.* It is soluble in alcohol. This solution has a bitter taste, and when mixed with one drop of a sugar solution (one part sugar to four of water) and pure conc. sulphuric acid added drop by drop (cooling whenever the mixture gets hot), it shows a yellowish tint, changing to pale cherry red, and eventually to an intense violet.—BILIARY ACIDS.

Group II.—*Calculi which leave a fixed residuë.*

A. The calculus gives with nitric acid and ammonia the reaction characteristic of uric acid (see *b.* p. 218).

To determine whether sodium, potassium, calcium, or magnesium be present in combination with this uric acid, notice the behaviour of the calculus when heated.

a. It melts.

α . It gives a deep yellow colour to the Bunsen flame.

—SODIUM URATE.

β . It gives a violet colouration to the flame.—POTASSIUM URATE.

—POTASSIUM URATE.

b. It does not melt.

α . After calcination calcium carbonate remains (recognisable by its effervescence with an acid, &c.)—

CALCIUM URATE.

β . After calcination the residue dissolves with *slight* effervescence in dilute sulphuric acid. This solution neutralised with ammonia gives on addition of sodium phosphate a white precipitate.—MAGNESIUM URATE.

B. The calculus does not give the characteristic uric acid reaction. Calcine a portion of the calculus and examine the residue.

a. The residue melts on heating.—It probably consists of CALCIUM OR MAGNESIUM-AMMONIUM PHOSPHATES.

α . The calculus does not effervesce with acids either before or after calcination. From a hydrochloric acid solution ammonia and ammonium oxalate both throw down a white precipitate.—CALCIUM PHOSPHATE.

β . During the calcination an ammoniacal odour is perceptible. The residue dissolves without effervescence in acetic acid; from this solution ammonia throws down a white crystalline precipitate.—MAGNESIUM-AMMONIUM PHOSPHATE.

These two phosphates may also be recognised by the reactions given under the head of examination of sedimentary deposits in urine (p. 219.)

b. The residue does not melt on heating. The calculus may contain CALCIUM PHOSPHATE, OXALATE, or CARBONATE.

a. The residue is white, and does not turn red litmus blue. Dissolved in a little hydrochloric acid and sodium acetate, and *one drop* of ferric chloride added, a dirty white precipitate (ferric phosphate) is formed. To the filtrate from this precipitate ammonium sulphide is added, and excess of iron thus removed; after filtration the addition of oxalic acid causes a white precipitate.—CALCIUM PHOSPHATE.

β. The calculus dissolves in the mineral acids without effervescence, but after calcination these acids dissolve the residue with evolution of carbon dioxide. The reactions detailed on p. 127 for calcium oxalate are also given.—CALCIUM OXALATE.

γ. Mineral acids dissolve the calculus with effervescence; from this solution neutralised with ammonia, ammonium oxalate throws down a white precipitate.—CALCIUM CARBONATE.

If doubt should arise as to the presence of any of these substances in a calculus, special confirmatory reactions must be resorted to.

APPENDICES.

A.—*Apparatus List.*

Test-tubes. Test-tube stand. Test-tube holder. Test-tube brush. Steel spatula. A small porcelain, horn, or platinum spatula is also very useful. Small Wedgwood mortar and pestle.

Three or four porcelain basins varying from 5 to 10 centimetres in diameter.

Half a dozen glass rods in length about 20 centimetres, rounded at the ends by slight fusion in the blow-pipe flame.

Half a dozen flasks ; these should include both ' Florence flasks,' which are round bottomed and have no lip, and also flat-bottomed lipped flasks. The sizes should vary from 100 to 500 c.c. capacity.

One or two clamps fitted with bosses

Metal stand with three rings.

Iron tripod stand.

One or two small Bunsen lamps about 4 in. high, and the tubes about $\frac{3}{8}$ in. diameter.

Wire gauze cut in squares.

Pneumatic trough ; the round stoneware troughs with perforated moveable beehives are very serviceable.

Small earthenware trays for holding gas bottles ; these may also be made of thin sheet zinc ; the lids of tin canisters will serve very well.

Gas bottles ; these bottles should be about 20 or 25 cm. high, and 5 to 7 cm. in diameter, with wide necks.

Deflagrating spoons.

Funnel-tubes ; these are sometimes called ' thistle-headed tubes.'

A separating funnel, with stop-cock, to hold about 100 c.c.

Filtering-paper.—Imitation Swedish will do very well for qualitative analysis. It will be found convenient to have the paper cut into circular pieces, having diameters varying from 2 to 8 centimetres

Caoutchouc tubing and corks ; the red or black tubing is preferable to grey, as it does not split so easily.

Glass-plates, also round pasteboard discs, for covering gas bottles &c.
Bell jar ; this should hold about 750 cb. cm.

Retorts ; one or two of capacities varying from 50 to 200 cb. cm.

Files, round and triangular.

Stout soda-water bottle.

Large test-tubes, 20 cm. long, $2\frac{1}{2}$ cm. diameter.

A few small beakers. Nos. 2 to 5 are the most convenient.

Glass tubing of various sizes.

A glass cylinder, about 40 cm. in height and 8 cm. in diameter.

A Wolff's two-necked bottle.

Calcium chloride tubes.

Pipettes, to hold 5, 10 and 20 c.c.

Crucibles of porcelain, crucible tongs and triangles, also a few
Hessian crucibles.

One or two candles.

Copper wire and a pair of pliers.

Platinum wire inoderately thick, about 40 cm. in length.

This list will be found to comprise the greater part of the necessary
apparatus.

B.—Reagent List.

The following chemical reagents are required in the first part of the
course.

Potassium chlorate.

Manganese dioxide.

Silver nitrate.

Flowers of sulphur.

Charcoal.

Amorphous phosphorus.

Lime water ; this is prepared by agitating recently slaked lime with
cold water, allowing the undissolved portion of the lime to subside and
drawing off the clear liquid ; it must be kept in a well stoppered bottle.

Granulated zinc, prepared by dropping molten zinc from a height
into cold water.

Strong sulphuric acid.

Nitric acid.

Hydrochloric acid.

Sodium chloride (common salt).

Powdered metallic antimony.

Turpentine.

Copper foil.

Ferrous sulphate.

Ammonium nitrate.
 Ammonium chloride.
 Caustic lime.
 Calcium carbonate (marble).
 Oxalic acid.
 Ammonia water.
 Caustic potash solution.
 Alcohol (methylated spirit).
 Sodium acetate and caustic soda.
 Potassium bromide.
 Potassium iodide.
 Ether.

Chlorine water ; prepared by passing chlorine gas into cold water until the latter smells strongly of the gas.

Starch paste ; prepared by boiling a small quantity of starch in water, and allowing the liquid to cool.

Iodine.
 Calcium fluoride (fluorspar).
 Mercury.
 Barium chloride solution.
 Platinum tetrachloride solution. (See p. 229, No. 24.)
 Benzene.
 Calcium chloride.
 Cane sugar.
 Iron pyrites.
 Potassium dichromate.
 Ink—writing and printers'.
 Carbon disulphide.
 Sodium carbonate.
 Sand, bees-wax, tapers, Turkey-red cloth and madder-dyed cloth.
 Asbestos.

The following reagents are required in the course of qualitative analysis.

I. *Ordinary Reagents.*

1. **Hydrochloric acid**: this is prepared by adding three parts of water to one part of the strong acid.

2. **Sulphuric acid**: one part of the strong acid is diluted with four parts of water, the mixture allowed to cool, and the clear liquid decanted from any white sediment of lead sulphate.

3. **Nitric acid**: one part of the strong acid diluted with three parts of water.

4. **Aqua regia**, prepared when required by adding four parts of strong hydrochloric acid to one part of strong nitric acid.

5. **Ammonia**: one part of strong liquor ammoniæ is diluted with three parts of water.

6. **Sulphuretted hydrogen**. This reagent is preferably used in the gaseous state, and must be prepared as required; it is advantageous, however, to saturate a bottle filled with water with the gas (passing it in until on shaking the bottle the smell of sulphuretted hydrogen is very apparent), and keep this closely stoppered and as much as possible out of the light.

7. **Ammonium sulphide**. Prepared by passing sulphuretted hydrogen through strong ammonia water until it ceases to give a precipitate with magnesium sulphate; a little sulphur may then be added, and the liquid diluted with one part of water.

8. **Ammonium oxalate**: one part by weight, is dissolved in twenty-four parts by measure, of water, and the solution filtered.

9. **Ammonium chloride**: one part by weight in eight measured parts of water.

10. **Ammonium carbonate**: one part in eight measured parts of water.

11. **Potassium ferrocyanide**: one part by weight in twelve measured parts of water.

12. **Sodium phosphate**: dissolve one part by weight, in ten parts by measure, of water.

13. **Barium chloride**: the same proportions as in the last.

14. **Magnesium sulphate**: one part in eight of water.

15. **Caustic potash, or soda**: one part in eight of water.

II. *Reagents less frequently used.—Special Reagents.*

1. **Tartaric acid**: this reagent is generally used in a saturated aqueous solution.

2. **Acetic acid**: glacial acetic acid may be diluted with about four parts of water.

3. **Sulphur dioxide** must be prepared (by heating copper clippings with strong sulphuric acid) when required.

4. **Oxalic acid** (generally used as a solid reagent): the solution is prepared by dissolving one part by weight, in twenty measured parts of water.

5. **Ammonium nitrate**: used in the solid state.

6. **Ammonium molybdate** in nitric acid: one part of ammonium

molybdate is dissolved by heating in three parts of ammonia, and the solution poured gradually and with continual agitation into twenty parts of dilute nitric acid (one part acid to one of water).

7. **Potassium ferrieyanide** : a solution of one part by weight of this salt in twelve parts by measure of water must be made when required for use. It decomposes slightly on keeping.

8. **Potassium nitrite** : prepared by saturating caustic potash (sp. gr. 1.27) with nitrous fumes—evolved by the action of eight parts of nitric acid (sp. gr. 1.4) on two parts of starch—filtering, evaporating to dryness and dissolving the dry salt in two parts of water.

9. **Potassium sulphocyanide** : one part in ten parts of water.

10. **Potassium chromate** : one part in eight parts of water.

11. **Potassium cyanide** : one part in eight parts of water.

12. **Sodium acetate** : dissolve one part in four parts of water.

13. **Borax** : employed in the solid state in flame reactions.

14. **Microcosmic salt** (sodium-ammonium-hydrogen phosphate) is also used as a flux.

15. **Calcium sulphate** : shake up the salt with cold water for a considerable time, and filter.

16. **Barium carbonate**, is mixed with water to the consistence of cream ; shake well before using.

17. **Ferric chloride** : prepared by dissolving recently precipitated ferric hydrate in pure hydrochloric acid, keeping the salt slightly in excess, the solution is diluted with an equal volume of water, and filtered. One part of the solid is dissolved in twelve parts of water.

18. **Lead acetate** : one part is dissolved in ten measured parts of water.

19. **Lead dioxide** : used in the solid state.

20. **Mercuric chloride** : one part in sixteen parts of water.

21. **Ammonio-copper sulphate**, is prepared by adding ammonia drop by drop to a tolerably strong solution of copper sulphate until the precipitate which forms is nearly all dissolved. Filter, and preserve the clear solution for use.

22. **Ammonio-silver nitrate** : prepared by adding ammonia to silver nitrate in the same way as directed above.

23. **Cobalt nitrate** : one part is dissolved in ten parts of water.

24. **Platinum tetrachloride** : spongy platinum, or platinum foil in little pieces is boiled in nitric acid, washed, and dissolved by heating with aqua regia ; the solution is evaporated to dryness on the water-bath, hydrochloric acid added, and the liquid again evaporated to dryness. The residue is dissolved in about ten parts of water and the solution filtered.

25. **Stannous chloride.** Dissolve the salt by boiling in strong hydrochloric acid, dilute with four parts of water, and keep the liquid in a stoppered bottle containing a little granulated tin.

26. **Sodium hypochlorite (chloride of soda).** Dissolve one part by weight of bleaching powder in one and one-sixth parts, by measure, of water, and shake this with a solution of two parts sodium carbonate (crystals) in about one-fourth part by measure of water; filter, and preserve the clear liquid for use.

27. **Nessler's reagent** is made by dissolving 5 grams of potassium iodide in 18 c.c. of water, adding a cold concentrated solution of mercuric chloride until the precipitate of mercuric iodide which forms just ceases to be dissolved on stirring. Now add an aqueous solution of caustic potash prepared by the solution of 15 grams of caustic potash in 30 c.c. of water. The liquid is diluted to about 100 c.c., and preserved in a stoppered bottle for use.

28. **Zinc and copper:** the former in small rods, the latter in thin slips, are required for certain tests.

29. **Litmus papers,** are either blue or red; the former are prepared by boiling one part of commercial litmus in six parts of water; filtering the solution, dividing the filtrate into two parts, neutralising the free alkali in one part by stirring with a glass rod dipped in dilute sulphuric acid until the liquid appears faintly red, and then adding the other part. Slips of unglazed paper are drawn through this solution and then hung on a thread, out of the way of acid fumes, until dry; these slips are kept in a stoppered bottle. Red litmus papers are prepared by soaking unglazed paper in a solution of litmus which has been reddened by stirring with a rod dipped in sulphuric acid.

30. **Turmeric papers** are prepared by soaking slips of paper in a solution made by heating one part of powdered turmeric root in six parts of dilute spirit of wine. The papers when dried have a pure yellow tint.

31. **Sodium Nitroferrocyanide.** 42.2 parts pulverised potassium ferrocyanide are mixed with 31.5 parts of nitric acid diluted with its own bulk of water. When the salt is dissolved, the liquid is poured into a large flask and heated in a water bath until it yields a dark green or slate-coloured precipitate with ferrous sulphate. The liquid is allowed to crystallise, filtered, neutralised with sodium carbonate, boiled, again filtered, and again allowed to crystallise: if crystals of sodium nitrate form these are removed, and the supernatant liquid is slightly evaporated and again allowed to crystallise.

C.—Preparation of Pure Reagents.

1. **Hydrochloric acid** may be purified by dilution and redistillation. In order to oxidise sulphurous acid the distillate is treated with chlorine water until the liquid turns starch paper moistened with potassium iodide blue. Commercial tin salt (stannous chloride) is now added in the proportion of five grams to every kilo. of the acid ; after standing for a day or two all the arsenic is separated. The acid is finally distilled after addition of a little sodium chloride.

2. **Nitric acid**, is freed from nitrogen peroxide by passing a current of carbon dioxide through the liquid heated nearly to the boiling point in a retort. A little potassium nitrate is then added, and the acid distilled. The distillate is tested from time to time with silver nitrate solution, and when a few drops diluted with water fail to become opalescent on the addition of the silver solution, the receiver is changed and the distillation continued until about four-fifths of the acid have passed over. To detect sulphuric acid a small quantity of the acid is treated with a drop of barium chloride and evaporated to dryness in a porcelain basin, water is added and the liquid is poured into a test tube ; the solution should not be in the least degree turbid.

The student will occasionally need to use the red fuming acid obtained by saturating the strongest nitric acid with nitrogen tetroxide. This acid may be prepared by mixing about three parts of starch in small pieces with 200 parts of pure nitre, and pouring over the mixture contained in a large tubulated retort, 100 parts of Nordhausen sulphuric acid previously mixed with 100 parts of the strongest oil of vitriol. The retort should be placed on a sandbath ; the distillation commences without extraneous heat ; if the nitre is not quite free from chlorides the first portions of the distillate must be collected apart. A gentle heat is applied to the retort so soon as the distillation slackens. The operation must be carried on in a draught-chamber or in the open air, and due care must be taken to condense the distillate. The entire process must be conducted at the lowest possible temperature, and not too quickly, or the distillate will be contaminated with sulphuric acid.

3. **Sulphuric acid** : ordinary oil of vitriol almost invariably contains lead, arsenic, iron, and oxides of nitrogen. The readiest method of obtaining it free from these impurities is to heat it with a small quantity of ammonium sulphate and manganese dioxide and distil it. About 700 c.c. of the strong acid are poured into a porcelain dish, from two to three grams of ammonium sulphate are added, and the acid is heated until it fumes strongly ; the oxides of nitrogen are in this manner destroyed. The liquid is allowed to cool, the manganese

dioxide added, and the dish again heated nearly to boiling with constant stirring; the arsenious oxide is thus converted into arsenic pentoxide. The acid is again allowed to cool and transferred to a retort of 1000 c.c. capacity and distilled, a few platinum-clippings being added to moderate the violent *successive* character of the ebullition. The retort must be supported over the naked flame; this should be so arranged as to heat the sides of the retort more than the bottom, whereby the tendency to 'bump' is diminished. The neck of the retort may dip directly into the condensing flask; the latent heat of sulphuric acid vapour is so small that no water is needed to assist the condensation.

4. Potassium hydrate. Caustic potash is not readily obtained pure. The commercial substance may be partially purified by dissolving it in strong alcohol in a stoppered bottle, allowing the insoluble matters to subside, drawing off the clear supernatant dark-brown liquid by means of a syphon, and evaporating it in a silver basin until dense white vapours make their appearance. The resinous matter formed by the action of the alcohol should be skimmed off the surface by a silver spatula or spoon, after which the oily liquid is poured on to plates, where it solidifies; it is quickly broken up and preserved in well-stoppered bottles. Its solution should be kept in bottles free from lead, since the alkali rapidly attacks flint-glass, dissolving out the lead oxide.

The purest form of the hydrate is obtained by igniting a mixture of one part of pure nitre with two parts of thin copper foil cut in small pieces; the mixture is arranged in alternate layers in a covered copper crucible and heated for half an hour to a moderate red heat. When cold the mass is dissolved out by boiling water, and the turbid solution poured into a long stoppered cylinder, in order that the copper oxide may subside. The clear solution is removed by a syphon and rapidly boiled down in a silver basin to the state of the oily hydrate.

Instead of metallic copper ferric oxide may be employed. This is prepared by igniting ferrous oxalate; it is mixed with the nitre in the same proportion as the copper. Through the lid of the crucible runs a tube passing nearly to the bottom, through which a stream of hydrogen is delivered. The crucible is exposed to a low red heat for about an hour; when cold the mass is boiled out with water, and the iron oxide allowed to settle. The clear solution of the hydrate is then evaporated in a silver basin as above described. The ferric oxide may be used repeatedly for the same operation.

5. Sodium hydrate. Very pure caustic soda may be obtained by the action of the metal on water. The solution is prepared by floating a silver dish containing a small quantity of water in a basin of cold

water, and adding the metal, cut in very small pieces, to the water in the metallic dish. Care must be taken to allow the liquid to cool after each addition of the metal, or violent explosions may result, and the solution may be projected from the dish. The solution should be prepared when required, if needed in small quantity only ; it is not advisable to attempt to manufacture more than a few grams at a time.

Sodium hydrate free from silica and alumina may be obtained by boiling purified sodium carbonate with a little silver carbonate in a silver basin, decanting the clear solution, sufficiently diluting it, and again boiling it, with calcined marble, in the silver dish ; the solution is filtered by pouring into a funnel, the stem of which is stopped with pieces of marble, and over which is placed a quantity of pulverised marble. It is advisable before pouring on the alkaline liquid to wash the marble once or twice with distilled water to remove the fine dust.

Impure sodium hydrate may be freed from sulphates and chlorides by exposing a concentrated solution to a low temperature when the hydroxide crystallises out with seven mols. of water. This hydrate melts at 6° ; by repeated fusions and solidifications it may be obtained perfectly pure.

6. **Sodium carbonate.** The soda of commerce consists principally of the salt $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$, which requires 62.7 per cent. of water ; in addition it generally contains small quantities of sodium sulphate, chloride sulphide, and thiosulphate, together with traces of calcium and magnesium salts. In order to purify it the salt is recrystallised once or twice from warm solutions, the solution being agitated to prevent the formation of large crystals, which are apt to enclose the impure mother liquors. The crystalline powder is thrown on to a funnel, drained by the action of the pump, and washed with small quantities of ice-cold water. Its solution should give no precipitate with barium chloride after acidification with pure hydrochloric acid, and it should afford only the faintest indication of chlorine when neutralised with pure nitric acid and tested with silver nitrate solution.

7. **Calcium chloride.** The residual solution obtained in the manufacture of carbon dioxide from marble and hydrochloric acid is neutralised, if acid, by the addition of fresh marble in small pieces, and a small quantity of milk of lime is then poured into the solution so as to render it distinctly alkaline. It is heated gently and set aside, in order that the precipitated oxides of iron, magnesia, &c., may subside. The clear liquid is drawn off by means of a syphon, acidified with hydrochloric acid, and evaporated to dryness in a porcelain basin, the residue broken up and heated to about 200° on a sandbath until hydrochloric acid fumes no longer make their appearance. The mass should be

broken up into small pieces (about the size of pearl-barley grains) and sifted from the fine powder, which may be worked up on a subsequent occasion. The pieces should be light, porous, and perfectly white. On solution they must not show the least trace of alkalinity.

8. **Soda-lime.** The specific gravity of a strong soda-ley is ascertained by means of the hydrometer, and its strength is calculated from the table given in the 'Manual of Quantitative Analysis.' A definite quantity is then measured off, poured into a clean iron pot, and mixed with small pieces of freshly burnt lime. The weight of lime added should be double that of the soda in the solution. The turbid liquid is evaporated to complete dryness with constant stirring, and the dried mass is heated to low redness in an iron or clay crucible, and then broken up into small pieces. The soda-lime should be sifted, and the fine and coarse powder preserved separately in well-stoppered bottles. For many purposes a mixture of pure sodium carbonate and calcium hydrate may be used instead of soda-lime.

10.—Tables.

1. TABLE OF SOLUBILITIES.—(See Table I., p. 166.)

This table is so arranged that the *bases* are placed at the heads of the columns, the *acids* with which they may be combined, at the side.

The figures refer to the various *menstrua* in which the salts are soluble. Thus :

- I. means soluble in water.
- II. means soluble in acids, but insoluble in water.
- III. means insoluble in both water and acids.

The solubilities of the more commonly occurring salts are indicated by large letters I. II. III., while those which are of less frequent occurrence have small letters placed after them—I, 2, or 3.

Some substances belong to more than one class—this is indicated thus : 1-2 means a substance difficultly soluble in water, but soluble in acids. 1-3 means a substance soluble with difficulty in water, the solubility of which is not increased by the addition of acids.

2-3 means a substance insoluble in water, and but slightly soluble in acids. The solubilities of the more commonly occurring double salts are given in a separate table. In this table a few of the simple and compound Cyanides are also enumerated.

A small number attached to the figure indicating the solubility of a substance, thus II₆ means that further information is given in the notes to the table.

BASES.

Acids and Halogens, &c.	Group I.				Group II. Div. 1.				Group II. Div. 2.			
	PbO II.	Ag ₂ O 2	Hg ₂ O II.	HgO II.	Bi ₂ O ₃ 2	CuO II. ₂	CdO 2	See Acids As ₂ O ₃ I.-II.	As ₂ O ₅ II.	SnO 2	SnO ₂ 2-3	Sb ₂ O ₃ 2 ₃
S . . .	2	2 ₃	II. ₁	II. ₁	2	2	2	II. ₃	II. ₃	2 ₆	2 ₆	2 ₇
Cl . . .	I.-III.	III.	II.-III.	I.	I.	I.	I	—	—	I.	I	I.
I . . .	II.	3	II.	—	—	—	I	—	—	2	I	—
SO ₄ . .	II.-III.	I.-III.	I-2	I.	I	I.	I.	—	—	I	—	—
NO ₃ . .	I.	I	I.	I.	I. ₀	I.	I.	—	—	—	—	—
PO ₄ . .	2	2	2	2	—	2	2	—	—	—	—	—
CO ₂ . .	II.	2	2	2	2	II.	2	—	—	—	—	—
BO ₃ . .	2	I	—	2	2	2	I-2	—	—	—	2	—
C ₂ O ₄ . .	II.	2	2	2	2	2	2	—	—	—	2	I-2
ClO ₃ . .	I	I	I-2	I	—	I	I	—	—	—	—	I
As ₂ O ₃ .	2	2	2	2	2	2	—	—	—	—	—	2
As ₂ O ₅ .	2	2	2	2	—	II.	—	—	—	—	—	2
C ₂ H ₃ O ₂	I.	I	I-2	I	I	I ¹¹	I	—	—	I	I	I
C ₄ H ₄ O ₆	2	2	I-2	2	2	I	I-2	—	—	I-2	—	I.
CHO ₂ .	I	I	I	—	I	I	I	—	—	2	—	—
C ₆ H ₅ O ₇	2	2	2	—	—	I	I	—	—	—	—	—

BASES. — *Continued.*

Acids and Halogens, &c.	Group III.				Group IV.				Group V.				Group VI.		
	FeO II.	Fe ₂ O ₃ II.	Cr ₂ O ₃ II.-III.	Al ₂ O ₃ II.	CoO II.	NiO II.	ZnO II.	MnO II.	BaO I.	SrO I.	CaO I.-II.	MgO II.	(NH ₄) ₂ O I.	Na ₂ O I.	K ₂ O I.
S . .	II.	II.	—	—	II, S	II, S	II.	II.	I.	I.	I.-II.	2	I.	I.	I.
Cl . .	I.	I.	I.	I	I.	I.	I	I.	I.	I.	I.	I	I.	I.	I.
I . . .	I	I	—	—	—	—	I	I	I	I	I	I	I	I	I
SO ₄ . .	I.	I.	I.	I.	I	I.	I.	I.	III.	III.	I.-III.	I.	I.	I.	I.
NO ₃ . .	I	I	I	I	I.	I	I	I.	I	I	I	I	I.	I.	I.
PO ₄ . .	2	II.	2	2	2	2	2	2	2	2	II.	2	I.	I.	I
CO ₂ . .	2	—	—	—	2	—	II.	II.	II.	II.	II.	II.	I.	I.	I.
BO ₃ . .	2	2	2	2	2	2	2	2	2	2	2	2	I	I.	I.
C ₂ O ₄ .	I-2	2	I	2	2	2	2	2	2	2	2	2	I	I.	I.
ClO ₃ . .	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I.
As ₂ O ₃ .	2	2	I	2	2	2	3	2	2	2	2	2	I.	I	I.
As ₂ O ₅ .	2	—	—	—	2	2	—	—	2	I	2	—	I.	I	I
C ₂ H ₃ O ₂ .	I	I.	I	I	I	I	I	—	I.	I	I	I	I.	I.	I.
C ₄ H ₄ O ₆ .	I-2	I.	I	I	I	—	2	I-2	2	2	II.	I-2	I.	I.	I.
CHO ₂ .	I	I	—	I-2	I-2	I	I	I	I	I	I	I	I.	I	I
C ₆ H ₈ O ₇ .	I	I	I	I-2	—	2	2	I	2	I	2	I	I	I	I

TABLE OF SOLUBILITIES.—No. 2.

<i>Cyanide of Potassium</i>	I.
<i>Ferrocyanide</i>	„	I.
<i>Ferricyanide</i>	„	I.
<i>Ferrocyanide of Zinc and Potassium</i>	II.
<i>Prussian blue</i>	III.

DOUBLE SALTS.

<i>Potassium-aluminium sulphate</i>	I.
<i>Aluminium-ammonium sulphate</i>	I.
<i>Potassium-ammonium tartar</i>	I.
„ <i>Sodium</i>	„	I.
„ <i>Ferric</i>	„	I.
„ <i>Antimony</i>	„	I.
<i>Sodium-ammonium phosphate</i>	I.
<i>Ammonium-copper chloride</i>	I.
„ <i>Mercury</i>	„	II.
<i>Platinum-ammonium</i>	„	I-3.
„ <i>Potassium</i>	„	I-3.

Notes to Table of Solubilities.

1. *Hydrochloric acid* converts *minium* into lead chloride, insoluble in excess of the reagent. Nitric acid dissolves it partially, but converts some of it into insoluble brown lead peroxide.

2. *Antimonious oxide*, soluble in hydrochloric, but insoluble in nitric acid.

3. *Silver sulphide*, soluble only in nitric acid.

4. *Mercurous and mercuric sulphides*, soluble only in aqua regia.

5. *Arsenic sulphides*, decomposed slightly by boiling strong hydrochloric acid, but decomposed and dissolved by nitric acid.

6. *Tin sulphides* are decomposed and dissolved by hydrochloric acid, nitric acid converts them into insoluble hydrates.

7. *Antimonious sulphide*, dissolves in strong hydrochloric acid.

8. *Nickel and cobalt sulphides*, much more easily decomposed and dissolved by nitric than by hydrochloric acid.

9. *Basic bismuth nitrate*, soluble in acids.

10. *Basic lead acetate*, partially soluble in water, completely so in acids.

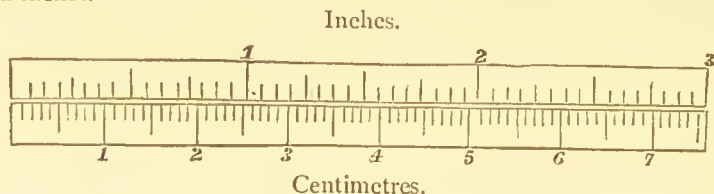
II. TABLE SHOWING THE RELATION BETWEEN ENGLISH WEIGHTS AND MEASURES AND THOSE OF THE METRIC SYSTEM.

	Measures of Weight.
Milligram	= 0.01543235 troy grains.
Centigram	= 0.1543235 " "
Decigram	= 1.543235 " "
Gram	= 15.43235 " "
"	= .643 pennyweight.
"	= .03216 oz. troy.
"	= .03527 oz. avoirdupois.
Kilogram	= 2.6803 lbs. troy.
"	= 2.20462 lbs. avoirdupois.
Metric Ton (1000 kilos.)	= 2204.62 " "

	Measures of Length.
Millimetre	= .03937 inches.
Centimetre	= .3937 "
Decimetre	= 3.937 "
Metre	= 39.37 "
"	= 3.2809 feet.
"	= 1.0937 yards.

Inch = 2.53995 centimetres. Foot = 3.04794 decimetres.
Yard = .91438 metres. Mile = 1609.32 metres.

The accompanying scale shows the relation between centimetres and inches.



III. TO CONVERT DEGREES FAHRENHEIT INTO DEGREES CENTIGRADE AND VICE VERSA.

$$(C.^{\circ} \times 1.8) + 32 = F.^{\circ}$$

$$(F.^{\circ} - 32) \div 1.8 = C.^{\circ}$$

IV. TO CONVERT DEGREES OF TWADDELL'S HYDROMETER INTO SPECIFIC GRAVITY.

$$(\text{Degrees Twaddell} \times 5) + 1000 = \text{sp. gravity.}$$

$$(\text{Sp. Gravity} - 1000) \div 5 = \text{degrees Twaddell.}$$

REACTIONS OF THE THIONIC ACIDS.*

Reagents	Dithionic Acid, $\text{H}_2\text{S}_2\text{O}_6$	Trithionic Acid, $\text{H}_2\text{S}_3\text{O}_6$	Tetrathionic Acid, $\text{H}_4\text{S}_4\text{O}_{10}$	Pentathionic Acid, $\text{H}_5\text{S}_5\text{O}_{12}$
Caustic Potash	No precipitate	No precipitate	No precipitate	Immediate precipitate of sulphur, redissolving gradually on standing, if not in large quantity and coagulated. No action.
Dilute hydrochloric acid	No action	Evolution of SO_2 and precipitation of S Immediate black precipitate, becoming white on standing	No action	At first yellow precipitate, turning white with excess of reagent on standing.
Mercurous nitrate	No precipitate	Yellow precipitate, soon becoming black	Yellow precipitate, gradually darkening	Yellow precipitate, gradually darkening; black on adding ammonia.
Silver nitrate	No precipitate	No brown colouration, even on standing. On warming, Ag_2S precipitated	Yellow precipitate, turning black on standing or on adding ammonia	Almost immediate brown colouration, becoming black on warming.
Ammoniacal silver nitrate	—	—	No dark or brown colouration, even on standing, <i>unless warmed</i>	At first yellow precipitate, gradually turning black on heating, with evolution of HCN .
Mercuric cyanide	No precipitate	Yellow precipitate, becoming white with excess of reagent	On warming, white precipitate	On warming, pale yellow precipitate.
Mercuric chloride	No precipitate	—	White precipitate of sulphur	White precipitate of sulphur.
Potassium sulphurate solution	—	—	Decolorised, even without addition of dilute H_2SO_4	Decolorised, even without addition of dilute H_2SO_4 .
Dilute solution of potassium permanganate	One drop, immediate brown precipitate	One drop, immediate brown precipitate, even in presence of dilute H_2SO_4	—	—

* Smith and Takamatsu, *Trans. Chem. Soc.* 1880, p. 608.

V. NAMES, SYMBOLS, AND ATOMIC WEIGHTS OF THE ELEMENTS.

Element	Symbol	Atomic weight	Observer
Aluminium .	Al	27.02	Mallet
Antimony .	Sb	120	Schneider ; Cooke
Arsenic .	As	74.9	Kessler ; Dumas
Barium .	Ba	136.84	Marignac
Beryllium .	Be	9.08	Nilson and Pettersson
Bismuth .	Bi	208.0	Dumas ; Schneider
Boron .	B	11.04	Berzelius
Bromine .	Br	79.76	Stas
Cadmium .	Cd	112.04	Lenssen
Cesium .	Cs	133.00	Johnson and Allen ; Bunsen
Calcium .	Ca	39.90	Erdmann and Marehand
Carbon .	C	11.97	Dumas and Stas ; Liebig
Cerium .	Ce	139.9	Marignac ; Robinson
Chlorine .	Cl	35.37	Stas
Chromium .	Cr	52.08	Siewert
Cobalt .	Co	59.0	Russell ; Somaruga
Copper .	Cu	63.12	Millon and Commaille
Didymium .	D	145 (?)	Brauner ; Marignac
Erbium .	E	168.9 (?)	Bahr and Bunsen
Fluorine .	F	19.0	Luca ; Louyet ; Moissan
Gallium .	Ga	69.8	Leeoq de Boisbaudran
Germanium .	Ge	72.3	Winkler
Gold .	Au	196.8	Thorpe and Laurie
Hydrogen .	H	1	Dumas
Indium .	In	113.4	Winkler ; Bunsen
Iodine .	I	126.54	Stas
Iridium .	Ir	192.5	Seubert
Iron .	Fe	55.9	Dumas
Lanthanum .	La	138.5	Cleve ; Brauner
Lead .	Pb	206.40	Stas
Lithium .	Li	7.00	Stas
Magnesium .	Mg	23.94	Dumas
Manganese .	Mn	55.0	Dewar and Scott
Mercury .	Hg	199.8	Erdmann and Marehand
Molybdenum .	Mo	95.8	Liechti and Kempe
Nickel .	Ni	58.6	Russell
Niobium .	Nb	94.0	Marignac
Nitrogen .	N	14.01	Stas
Osmium .	Os	190.3	Seubert
Oxygen .	O	15.96	
Palladium .	Pd	106.3	Berzelius
Phosphorus .	P	30.96	Schrötter
Platinum .	Pt	194.38	Seubert

V, *Names, Symbols, and Atomic Weights of the Elements*—cont.

Element	Symbol	Atomic weight	Observer
Potassium .	K	39·04	Stas
Rhodium .	Rh	102·7	Seubert and Koppé
Rubidium .	Rb	85·20	Bunsen ; Piccard
Ruthenium .	Ru	101·40	Claus ; Joly
Scandium .	Sc	44·0	Nilson
Selenium .	Se	78·8	Pettersson and Ekman
Silicon .	Si	28·3	Thorpe and Young
Silver .	Ag	107·67	Stas
Sodium .	Na	22·99	Stas
Strontium .	Sr	87·3	Marignac
Sulphur .	S	31·996	Stas
Tantalum .	Ta	182·00	Marignac
Tellurium .	Te	125·0	Brauner
Thallium .	Tl	203·66	Crookes
Thorium .	Th	231·87	Krüß and Nilson
Tin .	Sn	118·80	Bongartz and Classen
Titanium .	Ti	48·0	Thorpe
Tungsten .	W	184·00	Schneider ; Dumas ; Roscoe
Uranium .	U	239·0	Zimmerman
Vanadium .	V	51·35	Roscoe
Ytterbium .	Yt	173·0	Nilson
Yttrium .	Y	89·6	Cleve
Zinc .	Zn	65·5	Reynolds and Ramsey
Zirconium .	Zr	90·0	Marignac



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